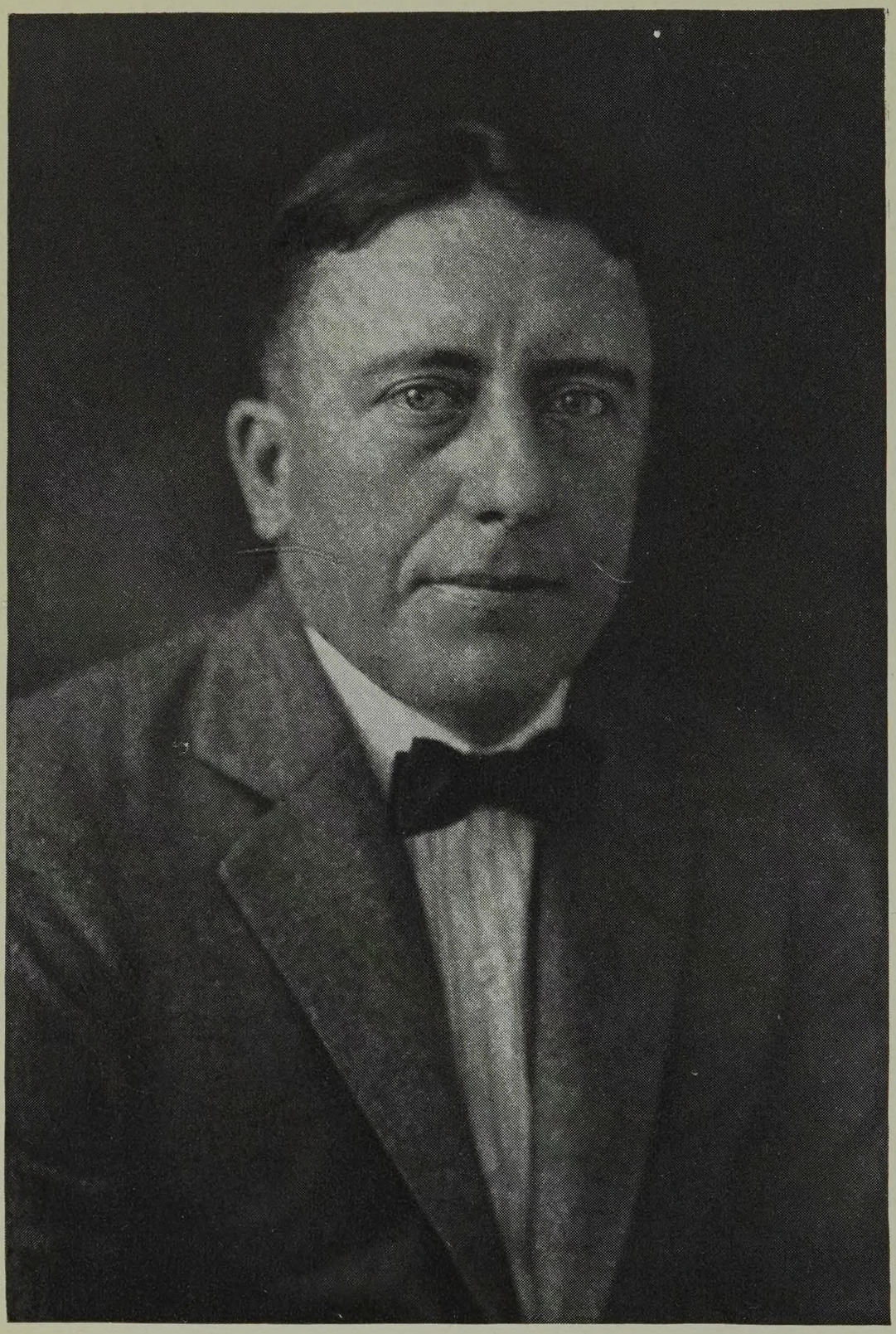
VOL. XLI 1922

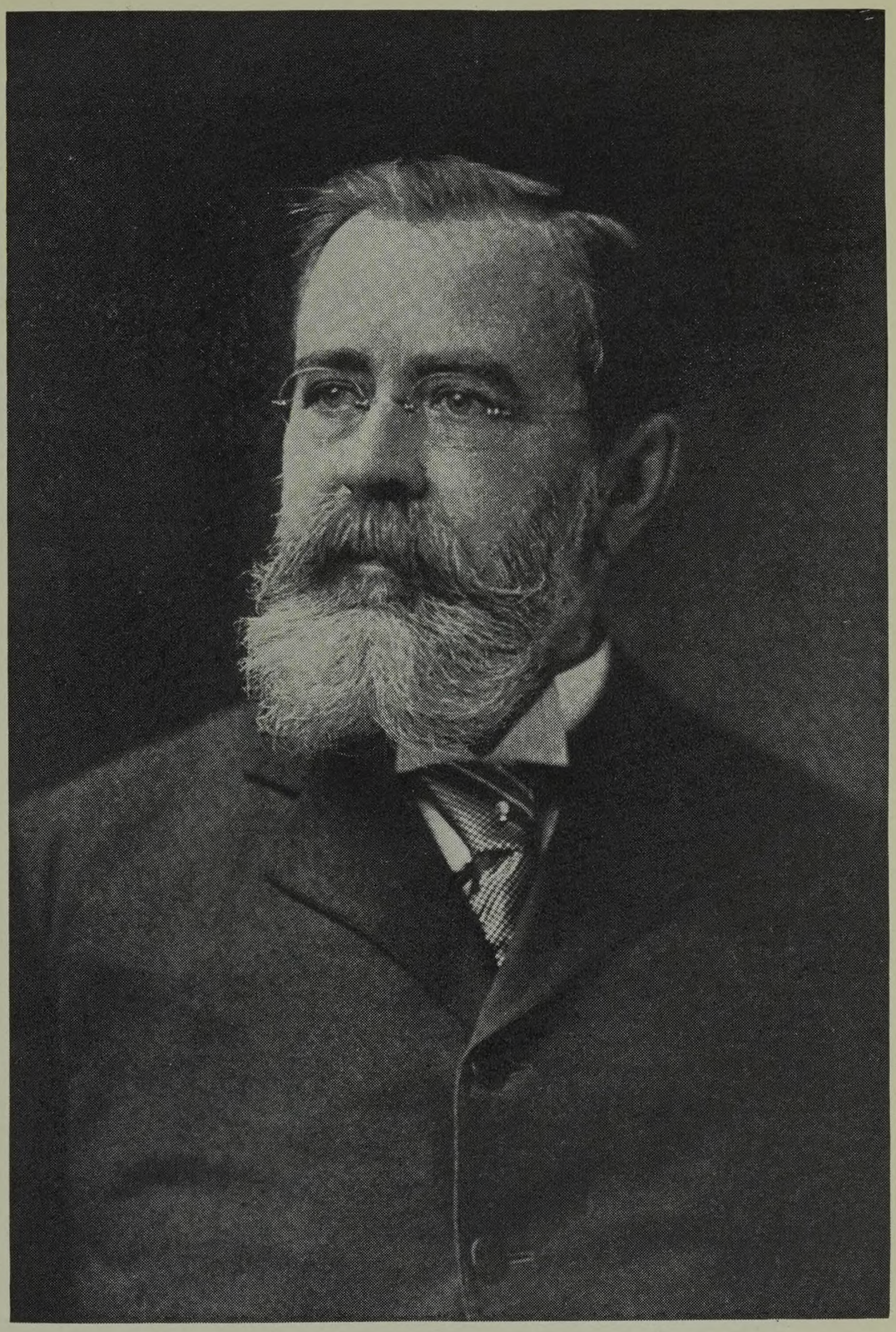
TRANSACTIONS of the American Electrochemical Society

LIBRARY
BRIGHAM YOUNG UNIVERSITY
FROM J. H. Smith
CALL NO. [redacted] ACC. NO. 25519

PERIODICAL



Carl G. Schluderberg



Carl Hering

TP
250
.E542

TRANSACTIONS

OF THE

American Electrochemical Society

BRIGHAM YOUNG UNIVERSITY
LIBRARY
PROVO, UTAH

VOLUME XLI

FORTY-FIRST GENERAL MEETING

BALTIMORE, MD.

APRIL 27, 28 AND 29, 1922

PUBLISHED BY

The American Electrochemical Society

AT THE OFFICE OF THE SECRETARY

COLUMBIA UNIVERSITY, NEW YORK CITY

1923

Copyright 1923 by the American Electrochemical Society.

Permission to reprint parts of the *Transactions* is hereby granted to current periodicals provided due credit is given.

This Society is not responsible for the statements and opinions advanced in papers or in discussion thereon.

Prices of Volumes I to XLI (excepting Vols. I, II, III, VII, XXIX and XXXI), to non-members $6.50 per copy; to members $4.00; to public libraries, colleges, scientific societies and journals, $4.00. Volumes I, II, III, VII, XXIX and XXXI, double above prices. Prices are for volumes bound in cloth, and include delivery within the postal union.

When the stock of any volume has been reduced to 25 copies (as Vol. III), the sale is limited to those purchasing the given volume as part of a complete set.

Complete sets will be sold to anybody at 25 percent discount on above prices; members may obtain the volumes necessary to complete their sets at 25 percent reduction on above prices.

WARE BROS. COMPANY, PRINTERS, ENGRAVERS
1010 ARCH ST., PHILA.

OFFICERS OF THE SOCIETY

PRESIDENT

C. G. SCHLUEDERBERG
Term expires 1923

PAST-PRESIDENT

ACHESON SMITH
Term expires 1923

VICE-PRESIDENTS

C. F. BURGESS
J. A. MATHEWS
E. L. CROSBY
Terms expire 1923

H. C. PARMELEE
A. H. HOOKER
W. S. LANDIS
Terms expire 1924

MANAGERS

G. K. ELLIOTT
H. B. COHO
F. J. TONE
Terms expire 1923

CARL HERING
J. V. N. DORR
F. A. J. FITZGERALD
Terms expire 1924

A. T. HINCKLEY
W. M. CORSE
WM. BLUM
Terms expire 1925

TREASURER

F. A. LIDBURY
Term expires 1923

SECRETARY

COLIN G. FINK, Columbia University, New York City
Term expires 1923

COMMITTEES

PUBLICATION COMMITTEE

F. A. J. FitzGerald, Chairman

Colin G. Fink, *Ex Officio*
Wm. Blum
C. B. Gibson
Terms expire 1923

C. G. Schluederberg, *Ex Officio*
A. T. Hinckley
H. C. Parmelee
Terms expire 1924

COMMITTEES—Continued

COMMITTEE ON LOCAL SECTIONS

F. J. Tone, Chairman — Colin G. Fink — C. G. Schluederberg

PATENT COMMITTEE

L. H. Baekeland, Chairman — F. G. Cottrell — E. J. Prindle

PUBLIC RELATIONS COMMITTEE

C. G. Schluederberg, Chairman

Colin G. Fink
W. D. Bancroft
Carl Hering
C. F. Burgess
E. G. Acheson
L. H. Baekeland
W. H. Walker
W. R. Whitney
F. A. Lidbury
Lawrence Addicks
F. A. J. FitzGerald
F. J. Tone
W. S. Landis
Acheson Smith

MEMBERSHIP COMMITTEE

A. T. Hinckley, Chairman

M. DeK. THOMPSON, Cambridge, Mass.
L. S. SAUNDERS, Worcester, Mass.
G. B. HOGABOOM, Waterbury, Conn.
H. C. PARMELEE, New York, N. Y.
C. F. ROTH, New York, N. Y.
E. F. KERN, New York, N. Y.
J. A. SEEDE, Schenectady, N. Y.
H. W. GILLETTE, Ithaca, N. Y.
G. H. CLAMER, Philadelphia, Pa.
R. E. ZIMMERMAN, Pittsburgh, Pa.
D. A. LYON, Washington, D. C.
P. J. KRUESI, Chattanooga, Tenn.
THEODORE SWANN, Anniston, Ala.
L. A. DREFAHL, Cleveland, O.
T. F. BAILY, Alliance, O.
G. K. ELLIOTT, Cincinnati, O.
W. K. BOOTH, Chicago, Ill.
O. P. WATTS, Madison, Wis.
E. L. CROSBY, Detroit, Mich.
J. W. BECKMAN, Oakland, Cal.
C. E. WILLIAMS, Seattle, Wash.
F. T. KAELIN, Montreal, Canada.
J. T. BURT-GERRANS, Toronto, Can.
J. G. BUTTERS, Hobart, Tasmania.
F. ANDERSEN, Trollhattan, Sweden.
HANS LANDOLT, Turgi, Switzerland.
B. BERG-HANSEN, Christiania, Norway.
K. B. QUINAN, W. Somerset, Cape Province, S. Africa.
C. A. KELLER, Paris, France.
H. E. ETCHELLS, Sheffield, England.
F. GIOLITTI, Torino, Italy.
YOGORO KATO, Tokio, Japan.
JEN CHOW, Shanghai, China.

WAYS AND MEANS COMMITTEE

H. B. Coho, Chairman

Lawrence Addicks
Colin G. Fink
Carl Hering
F. A. Lidbury
H. C. Parmelee

DIVISIONS OF THE SOCIETY

ELECTROTHERMIC DIVISION

Bradley Stoughton, Chairman

J. A. Mathews, Vice-Chairman — Colin G. Fink, Secretary-Treasurer

Directors

G. K. Elliott
James H. Parker
W. J. Priestley
Dorsey A. Lyon

DIVISIONS OF THE SOCIETY—Continued

ELECTRODEPOSITION DIVISION

George B. Hogaboom, Chairman

Chas. S. Witherell, Vice-Chairman Wm. Blum, Secretary-Treasurer

Directors

Lawrence Addicks F. C. Mathers
E. F. Kern O. P. Watts

FOREIGN REPRESENTATIVES

W. E. Hughes, England Bertram Wood, Australia

TECHNICAL COMMITTEES

PRIMARY BATTERIES

C. F. Burgess, Chairman D. L. Ordway

SECONDARY BATTERIES

P. G. Salom, Chairman O. W. Brown

ELECTRO ANALYSIS

H. S. Lukens, Chairman Geo. S. Forbes

RADIO ACTIVITY

S. C. Lind, Chairman H. S. Miner

CHLORINE AND CAUSTIC

E. M. Sergeant, Chairman Hugh K. Moore L. D. Vorce

CORROSION

Colin G. Fink, Chairman W. M. Corse W. D. Richardson

FIXED NITROGEN

W. S. Landis, Chairman Arthur B. Lamb Frank S. McGregor

WATER POWER

J. H. Harper, Chairman J. L. Yardley H. J. Pierce

ORGANIC ELECTROCHEMISTRY

C. J. Thatcher, Chairman Alexander Lowy

ELECTROCHEMISTRY OF GASEOUS CONDUCTION

Duncan MacRae, Chairman Wm. R. Mott

INSULATING OILS AND VARNISHES

H. C. P. Weber, Chairman

C. D. Hocker C. J. Rodman Christian Dantsizen

LOCAL SECTIONS OF THE SOCIETY

Philadelphia Section

Carl Hering, Chairman, Philadelphia, Pa.
S. S. Sadtler, Secretary, Philadelphia, Pa.

New York Section

C. A. Doremus, Chairman
W. A. Cowan, Vice-Chairman
H. B. Coho, Secretary-Treasurer

Pittsburgh Section

Earl Blough, Chairman, New Kensington, Pa.
C. B. Gibson, Secretary-Treasurer, Pittsburgh, Pa.

Niagara Falls Section

E. M. Sergeant, President, Niagara Falls, N. Y.
W. A. McKnight, Secretary and Treasurer, Niagara Falls, N. Y.

TABLE OF CONTENTS.

PAGE

Portrait of Dr. Carl Hering (Honorary Member).....Frontispiece
Portrait of President C. G. Schluederberg.....Frontispiece
Proceedings of the Forty-first General Meeting..... 1
Members and Guests Registered at the Forty-first General Meeting.... 13

PAPERS.

Presidential Address—The Technical Man as a Citizen—Acheson Smith. 15
Cast Iron as Produced in the Electric Furnace, and Some of Its Problems—George K. Elliott.....21
Synthetic Cast Iron—Jas. L. Cawthon, Jr..... 45
Synthetic and Electric Pig Iron Sanely Considered—Robert Turnbull.. 59
A Study of Carburization in the Manufacture of Synthetic Cast Iron—Clyde E. Williams and C. E. Sims..... 63
The Melting of Cast Iron in the Booth Rotating Electric Furnace—H. M. Williams and T. B. Terry..... 87
Electric Furnace Iron and Steel. Intermittent and Alternating Operations—W. E. Cahill..... 99
A Comparison Between Shaft and Open Top Furnaces in the Manufacture of Pig Iron Electrically from Iron Ore—R. C. Gosrow—109
The Electric Furnace in the Iron Foundry—Lyman C. Judson and Harry P. Martin.....127
A Plea for Rational Interpretation of Hydrogen Ion Measurements—William C. Moore.....137
Experiments with Alternating Current in Direct Current Electrolysis—W. B. Jones.....151
Conductivity of Copper Refining Electrolytes—Edward F. Kern and M. Y. Chang.....181
Corrosion by Electrolyte Concentration Cells—Robert J. McKay.....201
A Study of Effect of Impurities on Storage Batteries—Helen C. Gillette.217
Electrolytic Preparation of Ortho-Amidophenol—O. W. Brown and J. C. Warner 225
The Electrolytic Generation of Hydrogen and Oxygen with Special Reference to the Utilization of Off-Peak Power—Wm. G. Allan..239
The Production of Hydrogen by the Use of Silicon and Sodium Hydroxide—E. R. Weaver.....275

PAGE

A New Method of Determining the Radium Content of Carnotite Ores and Other Products of Low Activity—Victor F. Hess.....287

Electromagnetic Motions in Electric Furnaces—Carl Hering.....303

The Measurement of Pressures in Vacuum Type Electric Lamps—Duncan MacRae 311

Idiomorphic and Hyp-Idiomorphic Structures in Electro-Deposited Metal—W. E. Hughes.....317

The Acidity of Nickel Depositing Solutions—M. R. Thompson.....333

A Study of the Throwing Power and Current Efficiency of Zinc Plating Solutions—W. Grenville Horsch and Tyler Fuwa.....363

Hydrogen Overvoltage and Current Density in the Electrodeposition of Zinc—U. C. Tainton.....389

VOLUME XLI 1922

TRANSACTIONS

OF THE

American Electrochemical Society

PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTY-FIRST GENERAL MEETING OF THE SOCIETY, HELD AT HOTEL EMERSON, BALTIMORE, MD., APRIL 27, 28 AND 29, 1922.

The registration at this meeting totaled 202, of whom 125 were members and 77 guests.

PROCEEDINGS OF THURSDAY, APRIL 27, 1922

President Acheson Smith called the meeting to order at 9:30 A. M. and after a few words of introduction turned the meeting over to the Electrothermic Division and asked Messrs. Bradley Stoughton and A. T. Hinckley, who had planned and arranged for the "Electric Cast Iron" symposium to preside. Papers by George K. Elliott, W. E. Moore, J. L. Cawthon, Robert Turnbull, Clyde E. Williams and C. E. Sims were presented. These papers with discussions are printed in full in these Transactions. The Electrothermic Division reconvened at 2:30 P. M. for the presentation and discussion of "Electric Cast Iron" papers by the following: H. M. Williams and T. B. Terry, W. E. Cahill, R. C. Gosrow, L. C. Judson and H. P. Martin.

Some of the members of the Society took the opportunity during the afternoon to visit neighboring industrial plants, the list of which is included in the "Resolution of Thanks" in subsequent pages. There was also golf for those who wished to indulge in re-

creative sports, and to which the Maryland Country Club lent excellent facilities.

Dr. Hering made an Honorary Member.

On Thursday evening, at Johns Hopkins University, honorary membership was conferred upon Dr. Carl Hering of Philadelphia. Dr. Hering was one of the founders of the Society, and has been one of the most active and loyal members ever since. The first steps taken in organizing our Society took place in Dr. Hering's home. He has a world-wide reputation as an electrical engineer. He was born in Philadelphia, March 29, 1860, and received the degree of Doctor of Science from the University of Pennsylvania. He is a Chevalier Legion d'Honneur, past president of our Society, of the American Institute of Electrical Engineers, of the Philadelphia Engineers' Club, and an honorary member of the New York Electrical Society. He has contributed lavishly to the scientific world, and has published over 400 scientific and technical papers. He is the inventor of a number of electrical furnaces and other apparatus. His "Conversion Tables" are an international handbook. His scientific interests are diverse. He can discourse on almost any subject as freely as he can on the theory of Einstein or on the Steinmetz equations.

President Acheson Smith announced that Dr. Hering had been elected an honorary member and mentioned briefly his scientific attainments and his faithful work on the behalf of the Society over a period of twenty-one years. After the following endorsed communication was read the chairman introduced Dr. Hering, who expressed his appreciation of the honor which had been bestowed upon him.

To the Board of Directors, American Electrochemical Society.

Dr. Carl Hering of Philadelphia, is one of the founders of our Society, and one who has served the Society in a most unselfish and generous way, who has ever carried at heart the welfare and very best interests of our Society, who has contributed lavishly to our Transactions and who is recognized as one of the foremost engineers of the world.

Therefore, we the undersigned recommend Dr. Carl Hering

for honorary membership in our Society as a token of respect and sincere appreciation.

(Signed)

H. C. Parmelee
Acheson Smith
Colin G. Fink
H. B. Coho
Chas. A. Doremus
J. V. N. Dorr
E. W. Hale
C. B. Gibson
R. E. Zimmerman
Earl Blough
A. T. Hinckley
F. J. Tone
E. M. Sergeant
W. F. Hubley
W. A. Cowan
Atwood B. Oatman
Walter Wallace

After the close of the presentation Prof. R. W. Wood delivered a most fascinating lecture on "Fluorescence" with illustrations of many original experiments. Among other things he demonstrated his new glass, opaque to ordinary visible rays but transparent to ultra violet rays. Following this lecture there was an informal dance at the Engineers' Club.

PROCEEDINGS OF FRIDAY, APRIL 28, 1922

At 9:30 A. M. President Acheson Smith opened the annual business meeting of the Society. Secretary Fink read the report of the Board of Directors, including that of the secretary. In the latter the early death of Dr. Joseph W. Richards was commented upon at length. At the suggestion of Dr. Hering, the membership rose for a moment's silence in honor and memory of the late secretary of the Society. The report of the treasurer was read by Dr. Hering in the absence of the treasurer. These reports are appended to the Proceedings.

Among the several reports read by the secretary and of considerable interest to members was that of the Committee on Patents of the Society, submitted by Messrs. L. H. Baekeland, Chairman, F. G. Cottrell and E. J. Prindle. Official announcement was made therein of the passage of the Lampert Patent Office Bill, passed by the Senate on February 14 and signed by the President on February 18, 1922. This bill increases the appropriation for the Patent Office by nearly half a million dollars and affords relief

at a time when the Patent Office was "breaking." The members of our Society were very gratified and pleased with the report. Upon motion it was unanimously passed that a vote of thanks be expressed to Dr. Baekeland and his Patent Committee, who worked indefatigably to bring about the passage of the Lampert Bill.

REPORT OF COMMITTEE ON PUBLICATIONS

To The Board of Directors, American Electrochemical Society.

Dr. Colin G. Fink, having been appointed secretary to fill the unexpired term of the late Professor Richards, F. A. J. FitzGerald was designated as chairman of the Committee on Publications in December, 1921, and the present report covers your committee's activities since that date.

A total of 33 papers has been received, but of these two were too late to be considered. The results of the examination of the 31 papers received in time for the spring meeting were as follows:

Accepted	15
Accepted after revision	9
Rejected	7
	31

(Signed)

F. A. J. FitzGerald, Chairman.
Committee on Publications.

The Chair then read the

REPORT OF TELLERS OF ELECTION

The following is a list of votes cast in the election of officers for the year 1922-1923:

President: C. G. Schluederberg 261; O. P. Watts, 2; F. A. Lidbury, 1.

Vice-Presidents: H. C. Parmelee, 248; A. H. Hooker, 236; W. S. Landis, 233; R. E. Zimmerman, 67; W. M. Corse, 1; C. B. Gibson, 1; F. A. Lidbury, 1; C. G. Schluederberg, 1.

Managers: A. T. Hinckley, 218; W. M. Corse, 199; Wm. Blum, 164; G. B. Hogaboom, 81; C. B. Gibson, 77; A. W. Bur-

well, 33; Vaughn, 1; H. C. Parmelee, 1; A. H. Hooker, 1; W. S. Landis, 1.

Treasurer: F. A. Lidbury, 261.

Secretary: Colin G. Fink, 148; G. A. Roush, 123.

Void ballots: 32.

(Signed)

ALLISON BUTTS
BARRY MACNUTT,
S. S. SEYFERT

The President announced the following elections, as the result of the report of the Tellers:

President: C. G. Schluederberg.

Vice-Presidents: H. C. Parmelee, A. H. Hooker, W. S. Landis.

Managers: A. T. Hinckley, W. M. Corse, Wm. Blum.

Treasurer: F. A. Lidbury.

Secretary: Colin G. Fink.

In the absence of President-elect C. G. Schluederberg, who was on his return from a business trip to South America, the Chair asked Vice-President Hinckley to act as Chairman. The scientific business of the meeting then began with an address by the retiring president, Acheson Smith, on "The Technical Man as a Citizen." This was followed by the reading and discussion of papers by the following: Wm. C. Moore, W. B. Jones, E. F. Kern and M. Y. Chang, R. J. McKay, Helen C. Gillette, O. W. Brown and J C. Warner, W. G. Allan, E. R. Weaver. All of these papers with discussions are printed in this volume.

Through the efforts of the local committee, a very delightful boat trip on the steamer Latrobe had been arranged for Friday afternoon. Luncheon was served on board, and two stops were made—one at the U. S. Industrial Alcohol plant, which is one of the largest of its kind in the world; the second at the plant of the Davison Chemical Co. At the latter plant several demonstrations of unusual interest were made showing the great commercial possibilities of silica gel.

In the evening the members attended the complimentary smoker

given by the chemists and engineers of Baltimore, at the Engineers' Club. The entertainment included a talk on "Heredity" by Prof. Roscoe R. Hyde, who very cleverly illustrated his subject with the aid of charts and diagrams.

PROCEEDINGS OF SATURDAY, APRIL 29, 1922

The session was called to order at 9:30 A. M. by the President and announcement was made of the election of officers of the two divisions of the Society for 1922-1923:

Electrothermic Division

Chairman: Bradley Stoughton.

Vice-Chairman: John A. Mathews.

Secretary-Treasurer: Colin G. Fink.

Directors: George K. Elliott, James H. Parker, W. J. Priestley and Dorsey A. Lyon.

Electrodeposition Division

Chairman: George B. Hogaboom.

Vice-Chairman: Chas. S. Witherell.

Secretary-Treasurer: Wm. Blum.

Directors: Lawrence Addicks, E. F. Kern, F. C. Mathers and O. P. Watts.

Foreign Representatives: W. E. Hughes, England; Bertram Wood, Australia.

The technical session was then pursued by the reading and discussion of papers by the following: Victor F. Hess, Carl Hering, Duncan MacRae, W. E. Hughes, M. R. Thompson, W. G. Horsch and T. Fuwa, U. C. Tainton. These papers with discussion are included in the present volume.

Mr. M. C. Gilman, of Winnipeg, briefly described the exceptional opportunities for the exploitation and development of the electrochemical industry in western Canada. Raw materials, good transportation facilities, plentiful labor, and an abundance of hydroelectric power are some of the outstanding features of that district.

Upon the completion of a third hydroelectric power development in Winnipeg, 320,000 H. P. will be available, still leaving

undeveloped 250,000 H. P. for future requirements. The capital expenditure involved will be $70 per H. P., or between one-third and one-half the cost of the Niagara power plants.

Mineral deposits essential to the production of cyanamide, carbides, ferro-alloys, acetic acid, magnesium, aluminum, etc., are all available within economic distance of Winnipeg. These advantages in addition to others are difficult to duplicate elsewhere.

Dr. Carl Hering offered the following resolution of thanks which was heartily endorsed and unanimously adopted:

Resolution of Thanks

Resolved: That the American Electrochemical Society, in this its Forty-first Meeting, expresses its appreciation of the very successful efforts of its hosts in Baltimore to provide comfort and entertainment to the members, and extends a vote of thanks to the following:

Prof. R. W. Wood, for his very interesting lecture.

Prof. Roscoe R. Hyde and others, for providing entertainment at the Smoker.

The Engineers' Club.

The Maryland Country Club and Baltimore Country Club.

The Harbor Engineer, for the use of the steamer Latrobe.

The U. S. Industrial Alcohol Co.

Davison Chemical Co.

Baltimore Copper Works.

American Refractory Co.

Maryland Glass Corp.

Emerson Drug Co.

Standard Oil Co.

Howard Refractory Co.

Bethlehem Steel Co.

Standard Guano Co.

Hendler Creamery Co.,

and especially to the very active and efficient local committee, including the ladies' committee, as also to the weather gods for keeping up the reputation of the meetings of this Society to be favored with good weather.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

The following are some of the important items of business transacted by your Board of Directors during the past year:

The proposed By-Laws concerning Divisions of the Society were adopted as printed in Section 11 of the By-Laws, Volume 39.

In February the Society participated in the reception of Madame Curie upon her visit to the United States.

A new By-Law, that "At the annual meeting of the Society at least one session be devoted to the subject of Electrothermics" was adopted after considerable discussion. (Section 10, By-Laws, Volume 39).

At the September meeting of the Board, it was moved and passed that the price of the bound Transactions to members be fixed at $8.00 for the 1922 volumes, and at the same rate, $4.00 per volume, as the base price for previous volumes. To further increase the income of the Society, the sale price of volumes to non-members was fixed at $6.50 per volume and to Libraries at $4.00 per volume.

The Board authorized the formation of an Electrodeposition Division of the Society, the organizing committee of which consisted of Messrs. Wm. Blum, Chairman, George B. Hogaboom and H. S. Lukens.

We very much regret to record the death of Prof. Joseph W. Richards, secretary of the Society for over 15 years, a loyal, ardent worker of the Society ever since its inception. As tribute in honor of this indefatigable worker the Society held a memorial meeting in New York, November 16, 1921. See volume **40,** 4 (1921.)

The question of issuing the Society's publications monthly with the object of eliminating the publication of bound volumes of the Transactions was carefully considered and discussed, but found to be inadvisable for immediate adoption.

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1921 the Society held two general meetings, one at Atlantic City, April 21, 22 and 23, at which the attendance was 104 members and 61 guests, total 165; the second at the Lake Placid Club, N. Y., September 29, 30 and October 1, at which the registration was 65 members and 48 guests, total 113. The Transactions of the spring meeting, the feature of which was the "Corrosion" Symposium, include 31 papers, and those of the fall meeting, embodying a Symposium on "Non-ferrous Metallurgy," 30 papers.

Volume XXXVIII, covering the Transactions of the Cleveland Meeting, was distributed to members during October of last year.

The edition of Volume XXXVIII was as follows: 1650 copies complete, bound in cloth, 350 copies bound in paper for distribution to the Faraday Society, 250 copies unbound to be kept in stock, and 50 extra copies of each paper, with discussion, for distribution in pamphlet form to authors of papers.

The stock of Volumes on hand December 31, 1921, was as follows:

Volume I, 82; II, 102; III, 12; IV, 286; V, 220; VI, 245; VII, 183; VIII, 337; IX, 341; X, 324; XI, 227; XII, 254; XIII, 206; XIV, 402; XV, 370; XVI, 415; XVII, 449; XVIII, 599; XIX, 483; XX, 459; XXI, 489; XXII, 437; XXIII, 455; XXIV, 484; XXV, 545; XXVI, 515; XXVII, 413; XXVIII, 507; XXIX, 102; XXX, 436; XXXI, 85; XXXII, 316; XXXIII, 296; XXXIV, 309; XXXV, 565; XXXVI, 608; XXXVII, 409; XXXVIII, 825; Index 1-20, 585.

Condition of Membership of the Society in 1921.

Members January 1, 1921	2279	
Qualified as members in 1921	120	2399
Deaths in 1921	10	
Resignations in 1921	91	
Dropped for non-payment of dues in 1921	126	227
Members, December 31, 1921		2172
Net decrease for calendar year		107

Condition, April 27, 1922.

Members January 1, 1922	2172	
Qualified as members to April 27, 1922	47	2219
Deaths	3	
Dropped for non-payment of 1921 dues	221	224
Members April 27, 1922		1995
Members April 21, 1921		2220
Net decrease		225

Financial Statement.

The statement of receipts and expenditures, investments, accounts receivable and payable, as of December 31, 1921, listed below were audited and established as being accurate by Miller, Franklin, Basset and Co., auditors and public accountants of New York.

Receipts in 1921

Cash Balance—January 1, 1921		$ 212.36
Receipts:		
Entrance Fees	$ 510.00	
Current Dues	7,533.54	
Back Dues	540.00	
Advance Dues, 1922	1,644.25	
Advance Dues, 1923	5.00	
Volumes—1920	265.00	
Volumes—1921	4,210.00	
Volumes—1922	1,204.00	
Volumes—1922	5.00	
Sale of Publications—Non-members	2,907.81	
Sale of Reprints	322.40	
Sale of Membership Certificates	12.00	
Sale of Society Pins	42.00	
Payment of 1919 Transactions by Faraday Society	430.41	
Subscription to Faraday Society Transactions	258.75	
Appropriation returned—Cleveland Local Committee	100.00	
Temporary Loan—J. W. Richards	1,000.00	
Sale of U. S. Victory Bond	986.23	
Interest on Liberty Bonds	363.75	
Interest on Philadelphia Electric Bonds	77.50	
Interest on Bank Balances	43.11	
Total Receipts		22,460.75
		$22,673.11

Expenditures in 1921

Publication Expenses:

Printing of Volume 37	$4,593.23	
Printing of Discussion—Volume 37	671.79	
Printing of Volume 38	454.41	
Preprints for Volume 39	2,610.15	
Preprints for Volume 40	610.43	
Engraving	605.00	
Extra Reprints	300.32	
Binding of Back Volumes	118.50	
Total Publication Expenses		$ 9,963.83

Office and General Expenses:

Secretarial Appropriation	$3,600.00	
Office Printing	464.80	
Office Postage	115.15	
Office Expense—Stationery, Supplies and Equipment	1,228.37	
Postage on Advance Copies and Bulletins	925.15	
Postage on Volumes	419.92	
Freight and Express on Volumes and Preprints	119.80	
Expenses of Meetings	1,101.41	
Society Pins	225.82	
Directory of Members	12.00	
Membership Certificates	4.10	
Membership Committee	33.31	
Publication Committee	17.34	
Booth Committee	75.00	
Local Sections	315.00	
Electrothermic Division	44.12	
Electrodeposition Division	16.45	
Contribution to Annual Table of Constants	75.00	
Storage and Insurance	379.40	
Total Office and General Expenses		9,172.15
Total Expenditures		$19,135.98
Cash Balance—December 31, 1921		3,537.13

Investments, Accounts Receivable and Payable

As of December 31, 1921

Investments:

Philadelphia Electric Company Bonds, 5's	$ 3,100.00
First Liberty Loan 4% Registered	2,000.00
Second Liberty Loan 4% Registered	2,000.00
Third Liberty Loan 4¼% Registered	2,000.00
Fourth Liberty Loan 4¼% Registered	2,000.00
Victory Loan Notes 4¾% Registered	1,000.00
Total Investments	$12,100.00

Accounts Receivable:

Members—Dues	$1,918.54	
—Volumes	970.00	
		$ 2,888.54
Non-Members—Publications		1,341.47
Total Accounts Receivable		$ 4,230.01

Accounts Payable:

Ware Bros. Company	5,586.57
Estate of J. W. Richards (Loan)	1,014.00
Total Accounts Payable	$ 6,600.57

Notes Payable:

Ware Bros. Company (due January 23, 1922)	$ 3,115.87

TREASURER'S ANNUAL REPORT, 1921

January 1, 1921, Cash Balance	$ 212.36	
Total Receipts, 1921	22,460.75	
		$22,673.11
Total Expenditures		19,135.98
Balance, December 31, 1921		$ 3,537.13
Balance in E. P. Wilbur Trust Co., 12-31-21	$ 3,429.24	
Balance in Commonwealth Trust Co.	256.49	
Balance in Cash Drawer	50.00	
		3,735.73
Less December, 1921, checks not in		198.60
Balance 12-31-21, as above		$ 3,537.13

We have examined the above statement of account, and receipts and expenditures for the year 1921, and find the same to be correct.

We also report investments of the Society in the Safe Deposit Vault of the Commonwealth Title Insurance and Trust Co., Philadelphia, Pa., as listed in the Financial Statement above.

(Signed) H. B. Pulsifer,
(Signed) H. B. Coho,
Auditors.

MEMBERS AND GUESTS REGISTERED AT THE FORTY-FIRST GENERAL MEETING

Members

Lawrence Addicks
Wm. G. Allan
W. Asef
Richard Bailey
W. D. Bancroft
A. F. Bang
Wm. Blum
Wm. H. Boynton
Frank W. Brooke
D. C. Burroughs
Allison Butts
F. K. Cameron
R. T. Chace
R. B. Chillas
G. H. Clevenger
H. B. Coho
E. A. Colby
E. F. Cone
W. M. Corse
G. E. Cox
E. L. Crosby
A. C. Cummins
G. L. Davison
Fred. W. Dodson
G. K. Elliott
Alex. L. Field
Colin G Fink
F. A. J. FitzGerald
Raymond Freas
John R. Freeman, Jr.
C. B. Gibson
H. W. Gillett
M. C. Gilman
G. C. Given
A. K. Graham
J. R. Griffith
Burr Hamilton
Carl Hering
Victor F. Hess
R. P. Heuer
A. T. Hinckley
Frank Hodson
B. B. Hood
A. H. Hooker
Karl Horine
W. G. Horsch
S. Francis Howard
R. R. Hyde
B. H. Jacobson
H. M. Johnquest
Louis Jordan
Lyman C. Judson
F. T. Kaelin
F. R. Kemmer
Ivor Kenway
C. J. Kryzanowsky
A. Kuhlmann
H. A. Lavene
F. A. Lidbury
S. C. Lind
R. A. Long
B. F. Lovelace
H. S. Lukens
D. A. Lyon
H. G. McIntosh
W. Wallace McKaig
R. J. McKay
H. S. McQuaid
P. A. McTerney
Duncan MacRae
Chas. P. Madsen
R. E. Maeder
W. W. Mann
H. P. Martin
E. J. K. Mason
R. K. Meade
J. E. Mills
H. S. Miner
Guy K. Mitchell
Richard Moldenke
Wm. C. Moore
Preston M. Nash
E. F. Northrup
J. D. Noyes
H. C. Parmelee
C. L. Parsons
L. A. Parsons
H. W. Porth
Chas. H. Proctor
O. C. Ralston
A. G. Reeve
Wm. J. Rich
Chas. F. Roth
Edwin W. Rouse, Jr.
G. A. Roush
B. H. Schubert
J. A. Seede
C. E. Skinner
Acheson Smith
H. N. Spicer
A. D. Spillman
M. E. Stewart
Wm. H. Stone
Bradley Stoughton
R. B. Swope
E. M. Symmes
Eikichi Takagi
I. P. Tashof
C. J. Thatcher
Chas. C. Thomas
M. R. Thompson
R. H. Tillman
F. J. Tone
R. Turnbull
M. Unger
A. H. Warth
Helen Gillette Weir
C. J. Wernlund
R. H. White
Clyde E. Williams
H. M. Williams
Roger Williams
H. A. Winne
J. B. Wise
R. E. Zimmerman

Guests

F. A. Allner, Baltimore, Md.
R. J. Anderson, Pittsburgh, Pa.
Mrs. Wm. Blum, Washington, D.C.
F. M. Boyles, Baltimore, Md.
Mrs. W. H. Boynton, Baltimore, Md.
J. R. Cain, Washington, D. C.
R. M. Carter, Baltimore, Md.
E. I. Clapp, Baltimore, Md.
Frank Clearwater, Waterbury, Conn.
J. T. Clisham, Baltimore, Md.
Mrs. E. A. Colby, Newark, N. J.
A. Concilio, Bethlehem, Pa.
A. D. Conley, Baltimore, Md.
P. W. Dalrymple, Baltimore, Md.
A. Erickson, New York, N. Y.
Mrs. A. Erickson, New York, N. Y.
Chas. H. Fielding, Baltimore, Md.
Mrs. Colin G. Fink, New York, N. Y.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
Miss Elizabeth Freas, Baltimore, Md.
Mrs. Raymond Freas, Baltimore, Md.
J. F. Gaffney, Baltimore, Md.
R. B. Gerhardt, Baltimore, Md.
Mrs. J. R. Griffith, Niagara Falls, N. Y.
E. T. Gusher, Detroit, Mich.
C. H. Hall, Jr., Baltimore, Md.
H. E. Haring, Washington, D. C.
John H. Herrick, Baltimore, Md.
T. B. Hine, Edgewood, Md.
W. M. Horsch, Newburyport, Mass.
Wm. M. Horsch, Newburyport, Mass.
B. Kurrelmeyer, Baltimore, Md.
Mrs. P. A. McTerney, Schenectady, N. Y.
O. B. Malin, State College, Pa.
J. R. Mardick, New York, N. Y.
A. E. Marshall, Baltimore, Md.
R. W. Milnes, Kenwood, N. Y.
Mrs. R. Moldenke, Watchung, N. J.
Mrs. W. C. Moore, Baltimore, Md.
H. B. Moses, Washington, D. C.
H. L. Moses, Baltimore, Md.
J. F. Myrick, Baltimore, Md.
A. E. Nissen, Baltimore, Md.
Mrs. H. C. Parmelee, New York, N. Y.
H. E. Patten, Edgewood, Md.
F. F. Poland, Baltimore, Md.
S. T. Powell, Baltimore, Md.
Mrs. S. T. Powell, Baltimore, Md.
V. H. Power, Baltimore, Md.
John D. Pugh, Baltimore, Md.
G. W. Quick, Washington, D. C.
H. S. Rawdon, Washington, D. C.
E. E. Reid, Baltimore, Md.
Mrs. W. J. Rich, Washington, D. C.
P. O. Rippel, Chicago, Ill.
G. J. Roche, Bethlehem, Pa.
Mrs. C. F. Roth, New York, N. Y.
Mrs. E. W. Rouse, Baltimore, Md.
W. T. Schneider, Baltimore, Md.
H. B. Siegmund, Baltimore, Md.
Mrs. H. B. Siegmund, Baltimore, Md.
Mrs. Acheson Smith, Niagara Falls, N. Y.
J. S. Speer, St. Marys, Pa.
Mrs. H. N. Spicer, New York, N. Y.
Mrs. Wm. H. Stone, Baltimore, Md.
R. K. Taylor, Baltimore, Md.
Mrs. C. J. Thatcher, New York, N. Y.
E. E. Thum, New York, N. Y.
Mrs. J. W. Trott, Niagara Falls, N. Y.
H. H. Tunis, Baltimore, Md.
L. Von Friesen, Stockholm, Sweden
Wm. W. Varney, Baltimore, Md.
F. J. Vosburgh, New Rochelle, N. Y.
E. A. Vuillemier, Carlisle, Pa.
A. E. Walden, Baltimore, Md.
Mrs. Josephine M. Warth, Baltimore, Md.
Mrs. H. A. Winne, Schenectady, N. Y.
R. J. Young, Philadelphia, Pa.

The Presidential Address presented at the Forty-first General Meeting of the American Electrochemical Society, in Baltimore, Md., April 28, 1922.

THE TECHNICAL MAN AS A CITIZEN.[1]

By Acheson Smith

Never in the history of our country has there been such a pressing need for an intelligent citizenry. The post-war problems are of such a nature that it is difficult to understand them, and consequently almost impossible correctly to solve them. Various solutions are offered for the same problem, and to the great mass of people, unfamiliar with the technical side of a question, a man with an unsound panacea will appear to be just as safe to follow as the man who is a real authority on the subject.

The tendency is to look to our Government for aid, and as governmental aid is usually legislative, all kinds of legislation is proposed or enacted. In the opinion of many our revenue laws can be made to contribute to the prosperity of the country, but their provisions always provoke controversy and the final enactment is usually a geographical and personal compromise. Our financial system is constantly subject to attack, and there is an effort being made at present to alter it so as to make money more plentiful. Laws relating to our agricultural, mineral, water-power and other natural resources should be drawn with the greatest care, for upon their wise development will depend much of the future wealth of the nation. Regulatory legislation is being urged more and more, and while its purpose may be laudable, the carrying out of such laws requires so many enforcement officers that we are adding a burden to ourselves which has a doubly bad effect. First, it requires the expenditure of a great deal of money to enforce such regulation, and secondly, it takes a large number of people who might be producers and places them squarely in the unproductive, official class.

Many other serious problems are before the country and the world, today. For instance, the supremacy of the white race is

[1] The terms engineer, chemist, technical men, etc., are used synonymously, and are meant to include all men working in pure and applied science.

being challenged by those whose color is black or yellow, and the white race can only maintain its position by raising the intelligence of its leadership.

It is perhaps natural, under our form of government, for the proletariat to put great faith in political laws, and to be blissfully ignorant of the fact that where such laws are not based upon sound economic principles they will sooner or later prove futile. The futility of political laws, when they are contrary to the economic needs, is well illustrated by the conditions now prevalent throughout eastern Europe. Much more could be said on this subject, but it will probably suffice to add that the future success and safety of our country will depend upon the intelligence of its leaders.

When Lord Macaulay wrote his famous letter, in which he expressed doubt about the ultimate success of Jeffersonian Democracy, he said that "such democracy would sooner or later destroy liberty." We are now evidently in the process of being tried to see if this Republic can endure. It is comparatively safe from external enemies, but if we do not act wisely and in conformity to sound economic law we may be destroyed by our own acts, in spite of our good intentions. The times, therefore, call for strong men; men who have knowledge, men who have been taught to reason and to be guided by fact. This type of man being demanded, none are better able to qualify than chemists, engineers and other technical men.

We often hear the statement that this is the Age of the Engineer, but it is possible that we don't understand the full significance of that phrase. The present advanced state of civilization is mainly due to the technical men. That we have more comforts and luxuries today than we could have had a hundred years ago, and at the same time have more leisure for study and recreation, is due to the greater productivity per man, due to labor saving devices, improved processes and administrative methods. If production per capita had not increased, we would have little time for the fine arts, and no means with which to sustain those who would devote their lives to such pursuits.

If we desire to visualize what the world owes to the technical man, all we have to do is to consider what would happen if our steam and electric power and all machinery and modern chemistry were taken away from us. We would have to reorganize society,

and each one would be so occupied in producing the necessities of life he would have no time to produce non-essentials, and very little if any time to enjoy them. The present standard of living among our laboring people is solely due to the engineer. For example: If a farmer is only able to produce enough to feed and clothe his family he has no time for the finer things of life and cannot afford any luxuries. If, however, he can produce twice as much as is necessary to feed and clothe his family, he will have a surplus with which he can purchase luxuries. The number of luxuries he can buy will depend upon their cost, and therefore the cheaper they can be produced the more he can purchase. We thus see that the greater productiveness of the farmer enables him to acquire luxuries, and the greater the productiveness of those who manufacture them the cheaper these will be, and therefore the more the farmer can purchase.

As the ability of the farmer and manufacturer to produce is largely dependent upon the implements and methods supplied by the engineer, we can see that upon him rests the responsibility for future progress and the credit for what has already been accomplished. Putting it another way: The greater our productiveness the fewer people it will require to produce the necessities of life, and therefore the greater number that can be spared to work in art, medicine and other pursuits that contribute so definitely to our pleasures and comforts. In fact, our present standard of living can only be maintained if we keep up our production, and it is certain that the standard of living cannot be raised unless we increase our production per capita. As our increased production is due to the technical men, we see that the whole material progress of the country depends upon progress in pure and applied science.

If the things that make life worth while are ours because of greater productivity, it follows that we should honor the producers and do everything we can to educate all to the necessity for producing beyond their needs. The greatest incentive so far discovered to induce people to produce beyond their immediate requirements is the principle of property rights. When a man knows he can enjoy the products of his labor he will produce beyond the needs of the day, but if he is in doubt about being protected in such a right he will be without the incentive to produce a surplus. Therefore, we as men who understand the tremendously serious

effect of withdrawing or endangering such right to the enjoyment of property, should guard it zealously as the bedrock of civilization. While it sounds rather utilitarian to preach the gospel of production and property rights, it should be remembered that culture and the finer things of life presuppose leisure, and the amount of leisure we possess is in direct proportion to the surplus of life's necessities which are produced per man.

In view of what has been accomplished by the engineer, it may sound strange to say that he is seeking recognition, but such is the case. Nearly every technical society has had meetings and papers on such subjects as the status of the engineer. Practically all of the technical publications have had articles lamenting that the technical man does not take his proper place as a citizen, and is not found in our legislative bodies. Comparatively recently a Federation of Engineering Societies was formed for the purpose of increasing their influence at Washington. Many articles could be cited wherein it is pointed out that the engineer should have greater recognition, and suggesting ways by which that very desirable end could be attained. It is evident that among the technical men of the country there is a feeling that they do not occupy as influential a position as they should.

If technical men are the leaders in science and industry, and no one will dispute that they are, and if they seek recognition it must be in civic and political fields. The question, therefore, arises: What can the engineer do to procure such recognition? The matter has been discussed at considerable length, and the engineer should now take definite action toward attaining the position he seeks.

If we distinguish between the effort to force recognition through strength of numbers, and the recognition gained by the profession through its individual members becoming influential, we shall see that recognition of a group or class is difficult to procure and more difficult to maintain, while recognition of individuals is a natural force which extends throughout our whole political system. It is not desirable that engineers exercise influence as a class, but that they as individuals gain a position of influence. The first would be artificial and uneconomic, while the latter would be desirable and perfectly sound, because the struggle for success as individuals builds character, while the success of a class does not.

If we examine the political organization of our country we shall find that overlapping spheres of influence exist, reaching from the humblest community to the highest official circles in Washington. An individual becomes active in the political and civic affairs of his own locality, and is brought into contact with other similar individuals, who together form the dominating group in the city. A few from each city make the controlling group throughout the state, and a group from the various states are the influential men in the nation. These men are the real leaders, and those who would take an active part in our body politic must be willing to work as these men are working.

We must realize that the political machinery which controls our government is an actual fact, and if we are to become influential in the nation's affairs we must recognize the rules of the game and play accordingly. We, therefore, see that the leaders in the country are those who do a citizen's duty and a little more, over a term of years, and as a result find themselves the influential men in their community. Here is an opportunity for the engineer to do his locality a substantial service, and at the same time put himself in a position of real influence in the state and nation.

Under a system of government where the illiterate and men of low ideals have an equal voice with the educated and men of high ideals, the only thing that can prevent liberty from destroying itself is intelligent leadership. The technical men of the country should, therefore, start to work, each in his own community, and see if we cannot in a generation or two raise the standard of leadership so that sound thinking shall become the dominating influence in our legislative bodies.

The engineer is justified in striving for a high degree of technical attainment, but he should not lose sight of the fact that if he does not have the ability to lead he will probably not get far in his chosen profession, nor in the civic field. The qualities of leadership must be developed and there is probably no better way to begin than by taking a minor part in political affairs, working in civic bodies and taking an active part in at least one technical society. A man who is not willing to give a portion of his time and talents to his technical society, has lost sight of the fact that by doing so he will develop himself as well as advance the interests of the profession. It is not what he takes in but what he gives out that con-

stitutes his contribution to the world's work, and unless a man can become constructive he cannot hope for success. By taking an active part in civic affairs he will benefit his home community, and at the same time be training himself to be a leader.

While it is quite necessary that a man make himself proficient in his chosen line of work and avoid such things as would seriously interfere with such development, he should remember that this is a government of and by the people, and if he does not do his share some one is doing it for him, and probably doing it less ably than he could do it. He might well heed the words of Herbert Spencer: "The man expending his energy wholly on private affairs, refusing to take part in public affairs, pluming himself on his wisdom in minding his own business, is blind to the fact that his own business is made possible only by the prosperity of all."

There is a great need for educated men in all strata of the field of civic and political endeavor, and the university trained men can render wonderful service if each one will do his part. If a technical man does not gain the position of influence he seeks, he either does not have sufficient ability or he is unwilling to do the necessary work. If, however, the engineer will remember that he is a citizen as well as a technical man, and develop himself by serving his own locality, he will some day be surprised and pleased to find that his influence extends beyond his community, and is perhaps felt throughout the nation. Thus by his personal attainment he will help in procuring deserved recognition for the technical profession.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, President Acheson Smith in the Chair.

CAST IRON AS PRODUCED IN THE ELECTRIC FURNACE, AND SOME OF ITS PROBLEMS.[1]

By George K. Elliott[2]

Abstract

The scant literature of electric furnace cast iron is reviewed, showing that the duplexing process probably first was used upon a commercial scale in a foundry at Cincinnati, Ohio. The conditions favorable to the electric furnace for cast iron are discussed, and a preference expressed for the duplex process with basic-hearth electric furnace. Desulphurization and deoxidization in the electric furnace are described. Problems involving sulphur, oxygen and other gases and impurities—all brought up by electric furnace practice—are discussed, and several lines of investigation suggested.

Since up to this writing all that has been published concerning electric furnace cast iron has emanated from scarcely more than one or two sources, the sketching of its history is handicapped by a paucity of those materials that are most necessary to the annalist who would cover fully and fairly his field. It is probable that after the results of the present symposium have been published there will be much new material available to the waiting chronicler. By electric furnace cast iron we refer in the present paper only to iron prepared in an electric furnace in a foundry for strictly casting purposes, and not to electrically produced pig iron from the ore nor to so-called synthetic pig iron prepared from steel turnings and similar scrap.

The literature is quickly reviewed. In England, W. H. Hatfield in his sterling book, "Cast Iron in the Light of Recent Research,"

[1] Manuscript received February 28, 1922.

[2] Chief Metallurgist, The Lunkenheimer Co., Cincinnati, Ohio.

hails the electric furnace as the foundry furnace *par excellence,* and "looks forward to the development of this type of furnace." This is in the second edition published in 1918, and evidently the electric furnace had not been used for cast iron in England up to that date. This still seemed to be the status in that country last September, when the writer presented a paper on this subject to the annual meeting of the Institution of British Foundrymen.[3] Although the discussion of the paper was quite exhaustive there was no mention of its use in the British Isles with the sole exception of Mr. J. R. Hyde, of Sheffield, who said he had put in an electric furnace about five years before, finding it "very interesting if not profitable." Evidently in England electric power costs stand in the way of the use of this type of furnace for any but very unusual iron castings. On the continent the use of the electric furnace for cast iron has been vaguely rumored, but probably this has been based largely upon the development during the war of the electric furnace process for making low-phosphorus pig iron from steel turnings.

In this country the electric furnace has been used much more extensively for cast iron, although the literature still is very meager. The first extended account of the use of the electric furnace for cast iron was in a paper read by the writer before this Society in April, 1919,[4] which was followed by several other papers touching upon various phases of the cupola-electric-furnace tandem or duplexing process described in the original paper.[5]

F. H. Bell, also writing in 1919[6] described a furnace melting four 625-pound heats in a 10-hour day, predicted the successful competition of even the cold-charge process with the cupola on account of the ease of handling special mixtures and the high quality of the product.

A Bureau of Mines bulletin issued in 1914[7] covering the whole field of metallurgical electric furnaces makes no mention of cast iron, indicating the electric furnace had not yet been there applied.

[3] "The Basic Hearth Electric Furnace and Some Problems of Cast Iron", G. K. Elliott; The Foundry Trade Journal (London) 1921, **24**, 236.

[4] "Improving the Quality of Gray Iron by the Electric Furnace," G. K. Elliott; Transactions of the American Electrochemical Society 1919, **35**, 175.

[5] "The Electric Furnace as an Adjunct to the Cupola"; G. K. Elliott; Transactions of the American Foundrymen's Association, **28**, 352. "A Note on the Electric Furnace and the Problem of Sulphur in Cast Iron"; G. K. Elliott; Transactions of the American Foundrymen's Association (1920).

[6] Can. Machinery **21**, 7.

[7] Bulletin 77, "The Electric Furnace in Metallurgical Work."

Moldenke in his admirable book[8] published in 1917 foresees the advent of the electric furnace in the iron foundry for the primary purpose of enabling the iron foundry to supply steel castings, and incidentally to run cast iron for high-quality work. He concludes his prophetic comment with the words. "It is quite possible that the not far distant future may see something practical developed of benefit to the foundryman." It is interesting to know that as he was writing, the prediction concerning the electric furnace was beginning to near realization in a plant at Cincinnati, Ohio. However it is evident that prior to 1917 the electric furnace had not been used for cast iron to the knowledge of the well informed authority just quoted. In February, 1921, he presented a keen and comprehensive paper upon the subject before the American Institute of Mining and Metallurgical Engineers[9] indicating that the electric furnace had by that time won a place for itself in the iron foundry.

The first use of the electric furnace for gray cast iron in every day production, and not in sporadic experimental heats, seems to have been in the iron foundry of The Lunkenheimer Company at Cincinnati in the summer of 1917. Beginning with "cold charge" heats the process soon underwent a logical change into the duplexing process, wherein the cupola was utilized for the otherwise costly melting period of the cycle. The first few months the furnace, a Heroult with basic hearth, was confined to melting cold charges of special low-phosphorus iron, desulphurizing, reducing the carbon by dilution with steel, adjusting silicon to suit the size and nature of the castings, and finally casting into parts for which semi-steel originally had been used.

This product perhaps came as near being the consummate semi-steel as is possible. This relatively expensive process soon developed into the tandem process and now is used only on rare occasions when small heats of special iron are desired. It is the writer's understanding that several foundries are using the cold-charge method regularly where tonnage is too small to justify a cupola, and close control of an exceptional grade of iron is required. Under such combination of circumstances there seems

[8] "Principles of Iron Founding," Richard Moldenke (1917).

[9] "Electric Furnaces in the Iron Foundry," Richard Moldenke; The Iron Age, Feb. 17, 1921, 437.

to exist a limited economical field for the complete cycle of melting, refining and superheating in the electric furnace.

Several of these "cold charge" furnaces are operating with acid hearth, which means leaving from the cycle the element of refining except in a sense that is mild in comparison with the rigorous basic process. Properly conducted this acid process consists of melting and superheating under conditions that at least are non-oxidizing as far as furnace atmosphere concerns. The length of stay in the furnace after being melted may become a period of purification, in so much as an undisturbed exposure to a high temperature in a harmless atmosphere is liable to bring about a flotation on the bath of some of its non-metallic inclusions. Especially will high sulphur aided by manganese automatically reduce in this way to a measurable degree. Irons with 0.15 percent sulphur have been known to decrease by as much as one-fourth or one-third through manganese sulphide floating to the surface.

The cold-charge process for cast iron probably never will acquire more than a scattered application, and the greatest possibilities seems to lie with the duplexing process. This is because the cupola cannot be relegated to disuse without working economic violence to the commercial foundry. The cupola delivers molten iron, with a minimum of care and labor, too cheaply to be discarded. Any melting scheme for the iron foundry must take into serious consideration the cupola furnace. It needs no substitute but at times an adjunct is desirable; here is the opportunity for the electric furnace.

Since the duplexing process apportions refining to the electric furnace the most logical hearth for the electric furnace is the most potently refining one, in other words, the basic hearth. In it lie the best and widest possibilities of the electric furnace for cast iron.

Duplexing as said before probably was practiced first at the Cincinnati plant, and there also it has been used most continuously, while it was at a plant in Birmingham, Alabama, that it developed its greatest tonnage. This was in a pipe foundry where frequently over 200 tons of iron were passed through the electric furnace in twenty-four hours.

"What are the conditions in the average iron foundry of today that make feasible the addition of an electric furnace to the

equipment?" This is a common question. In a sentence we can answer that the influencing factors are, (a) the limitations of the cupola, (b) the cost of available raw materials, and (c) a shifting of the basis of competition in a certain volume of the gray-iron castings business from price per pound to quality per piece. Any one of these may carry enough weight to swing the balances in favor of the electric furnace in some cases while in others—by far the great majority—the united three cannot budge the foundry policy from its present established position. The electric furnace must not be taken up hastily and without a complete survey of its advantages and disadvantages, because in one field it may be an unmistakable success while in another it will show only loss.

In speaking of the limitations of the cupola the writer must not be taken as unfriendly to it or in the least unappreciative of its many sterling virtues. It is without peer as an efficient, inexpensive, universally operated metallurgical servant for the production of molten iron. Probably no other furnace can melt similar metal at a fuel cost of seventy-five cents or lower per ton, which is what the cupola does steadily and with approximate satisfaction on all counts. It lacks only some of the refinements of operation frequently demanded by modern conditions. These occasionally demanded improvements are an ability to reproduce uniformly any desired composition of iron, a positive ability to refine in addition to melting, and an increased power to superheat. To accomplish refining the cupola is helpless while it has decided restrictions when it comes to superheating.

Just as the inability to refine and superheat are outstanding weaknesses of the cupola, so is the corresponding ability to do them the great advantage of the electric furnace, especially the furnace with basic bottom. Such furnace is the preeminent refining furnace for iron and steal. Handling cast iron, it is capable of delivering without too great attention metal superheated to any degree, reduced in sulphur as required, deoxidized, and with carbon, silicon and manganese adjusted to the desired standards. Phosphorus alone cannot be altered in cast iron by the electric furnace except by impracticable methods.

The electric furnace is at its best when coupled with a chemical laboratory in an intimate manner. By sampling the molten iron as soon as transferred from the cupola the laboratory can determine

as many elements as desired, and the proper additions can be made before the metal is ready to pour, making possible the closest regulation of the composition. Especially is this valuable in regulating silicon and carbon, elements reflected in the machinability of the castings. The rapidly growing tendency in machine shops to introduce standardized rates of machining seems to be taking little or no heed of the fact that there are many kinds of cast iron, and that more than one kind may come from one foundry in one cupola during one day.

Maintaining fixed rates of machining and high production cannot be divorced from a parallel preserving the fixed proper grade of iron in the castings. In order to keep uniformly a certain machinability, iron must not vary in composition over too wide a range, especially in silicon and carbon, and at times manganese. Not a few modern factories have installed ultra-modern castings-finishing methods without first co-ordinating in the proper way their metallurgical and mechanical operations. In such cases the results are liable to be either a sad falling down in production from what was so elaborately planned, or a sacrifice of highly desirable physical properties in the product in order to attain and preserve production. Planning production without first establishing the best grade of iron for the product has led to more than one manufacturing debacle. The combination of laboratory and electric furnace can be made to work nicely in solving problems of this order.

The most striking reaction taking place in the basic electric furnace is desulphurization; also it may become its most valuable. There is no gainsaying that there is a tendency towards higher sulphur in the world's scrap pile. This is not because the foundrymen are no longer afraid of it and are giving it free rein, but rather because it daily is becoming more difficult to hold it within bounds. The universal scrap pile is swollen with the grim harvest of the greatest of wars, and economy demands that it be worked over into usable implements fit for the pursuits of peace. The average of the sulphur is high, perhaps 0.15 percent, and upon remelting in the cupola almost 0.03 percent more is picked up with each remelt. The basic-hearth electric furnace seems created almost for this crisis. Elimination of sulphur by its means is one of the readiest of metallurgical operations. Cast iron of 0.18

percent can be reduced to under 0.07 percent in about thirty minutes, meaning the changing of relatively bad iron into good. Geographical considerations are strong here, and the foundry located in a region remote from the sources of good pig iron, and therefore having to rely upon the scrap pile of the neighborhood, may be in a logical position to consider seriously the basic-hearth electric furnace.

Illustrating this application of the furnace there was described in 1920 a small unit on the Pacific coast, in which a hand-fed, two-phase arc furnace was utilized for working up otherwise unusable iron scrap.[10] Tensile strengths of 40,000 to 45,000 pounds to the square inch (2.8 to 3.15 metric tons per sq. cm.) were claimed for the iron.

The introduction of the basic-hearth electric furnace is largely responsible for the prominence that the subject of sulphur in cast iron, especially low sulphur as compared with high, has received in recent years. The time is approaching rapidly when the question of the real effect of various amounts of sulphur in cast iron must be systematically and authoritatively investigated. Something is needed to reconcile the apparently anomalous results with high and low sulphur irons that are reported from time to time by different foundrymen and metallurgists. Logical sponsors for such inquiry would seem to be either the American Society for Testing Materials or the American Foundrymen's Association or a committee of the two organizations.

The conditions in cast iron that will conduce to the precipitation of sulphide, in particles of an optimum size and of an optimum degree of dispersion, so as to assist or at least not hinder the production of mechanical properties of a high order, is a subject about which we know practically nothing. In conducting a research along this line we can suggest a very promising means of attack in the recently announced slip interference theory of the hardening of metals by Jeffries and Archer,[11] which seems capable of a wide application to many of our metallurgical problems, including the one of sulphur in iron. The question of mechanical tests also is involved in the solution of the sulphur

[10] Electrical World; Anon; 1920, **75**, 265

[11] "The Slip Interference Theory of the Hardening of Metals," Zay Jeffries and R. S. Archer; Chemical and Metallurgical Engineering, 1921, **24**, 1057.

problem, and it seems advisable that increased attention be given to tests of a more dynamic nature than the customary transverse and tensile tests, because there is good reason for believing that tests of such nature will differentiate between irons that give nearly identical results under the mentioned static tests.

If an answer to the sulphur problem ever is found, it probably will be many-fold with different limits of sulphur for different kinds of castings. The writer has first-hand knowledge of one class of large castings that invariably are "dirty", to quote the foundryman, at an important machined point whenever sulphur reaches 0.10 percent or over. Empirically in this one case the answer has been found; generally we can only surmise how far we dare go with sulphur.

To the writer it seems that the sulphur question is involved in the greater one of general refinement, and it is probable that iron high in sulphur also is endowed plenteously with other impurities some of which may be almost entirely unknown. Examples are oxygen in various combinations, nitrogen as nitride, and perhaps others even less familiar. The fact that an iron is desulphurized is evidence that it has passed through a strong refining treatment, and the possibility that some of the benefits attributed to low sulphur in reality may be the result of the removal of one or more other impurities along with it, has to be recognized. Desulphurization of iron means one of the most drastic cleansings known to metallurgy and consequently low sulphur is becoming a hall-mark of refinement.

Removal of sulphur requires a reducing slag and this carries with it additional advantages to the iron. Broadly speaking there are two inflexible requirements to be complied with before desulphurization can take place—a strongly basic slag and complete deoxidation of slag and bath. Without both there is no elimination of sulphur. The slag is made from an excess of lime with fluor-spar added for fusibility, and coke dust to produce the needed reducing conditions. Deoxidation of bath, since manganese, silicon and carbon all are present, perhaps is a somewhat complex reaction, but for simplicity we can assume the probable role of manganese as illustrative. In this case the reaction can be taken as

$$FeO + Mn = MnO + Fe$$

Being not as soluble in molten iron as FeO, the MnO rises to the surface to be taken up by the slag, where it is acted upon by the carbon and reduced back to metallic manganese—

$$MnO + C = Mn + CO$$

the carbon monoxide escaping into the furnace atmosphere. After the last of the oxide has been removed from the slag the first step toward desulphurization begins. Immediately around the electrodes where the greatest temperature prevails the carbon and the lime of the slag react, forming calcium carbide—

$$CaO + 3C = CaC_2 + CO$$

This reaction is assurance that deoxidation is completed. Elimination of sulphur then proceeds by one or probably both of the following reactions—

$$\left.\begin{matrix} MnS \\ FeS \end{matrix}\right\} + CaO + C = \left.\begin{matrix} Mn \\ Fe \end{matrix}\right\} + CaS + CO$$

and

$$\left.\begin{matrix} 3MnS \\ 3FeS \end{matrix}\right\} + 2CaO + CaC_2 = \left.\begin{matrix} 3Mn \\ 3Fe \end{matrix}\right\} + 3CaS + 2CO$$

The calcium sulphide formed in either reaction is insoluble in molten iron, making certain the efficacy of the operation.

Deoxidation we have seen is a necessary concomitant of desulphurization, and cast iron coming from this process should be fairly free from oxides. This introduces one of the moot questions of cast iron. By some reputable authorities it is stoutly maintained that molten cast iron contains too much carbon, silicon and manganese to be able to carry iron oxide at the same time. Others declare it is entirely possible and that its presence has certain tangible effects. As to the nature of the effects again there is a division of opinion. One group claims they are good while another takes the opposite view, roundly condemning oxidized or "oxygenated" iron. The writer inclines to the belief that oxygen often persists in cast iron, in spite of the presence of oxidizable elements that should remove it, and also that its presence is undesirable. It seems to him that the persistence of oxygen as iron

oxide in molten iron is as reasonably expected as is the well known persistence of determinable amounts of sulphur and phosphorus in steel heats that have been put through the most rigorous and theoretically impeccable treatments for their removal. It is readily explained by the law of mass action, which enables the iron to hold to the last traces of these impurities.

That the influence of oxygen on the whole is bad, is borne out by many experiences with the product of badly acting or carelessly operated cupolas. In these cases the iron without doubt was exposed to oxidizing conditions, and that it was materially affected thereby was shown in the sluggishness of the melt, which in spite of a high temperature prevented its running out castings solid enough to pass a porosity test. It appears probable that oxygen in some of its combinations, especially iron oxide, raises the freezing point of cast iron, bringing about a practical diminution of fluidity. One other point against iron oxide is its reaction with carbon which is known to produce unsoundness in steel through the resultant gas, and there is reason to hold that this can happen also with cast iron. The time spent in the electric furnace during duplexing gives ample opportunity for this reaction to complete itself. This may be one of the substantial benefits of the process.

A novel and interesting, if not entirely acceptible, conception of cupola iron is presented in a recent article,[12] in which the theory is advanced that much of the supposedly oxidized iron from the cupola and other furnaces is not suffering from over-oxidation, but from the absorption of aluminum from the refractories, the same forming a carbide which, upon reacting with the moisture of the moulds, creates a gas with consequent blow holes in the castings. The article also claims an analogous reaction can take place at electric-furnace temperatures, with the absorption of calcium from the basic slag and the formation of carbide in the metal. Following out this assumption, the claimed benefits of oxygenated iron are traced to the curative effect that oxygen naturally would have upon iron contaminated with carbides. While the present writer has not had the opportunity to investigate this strange theory which presupposes deoxidizing in the cupola, he is not able to make it account for many of the cases of apparently

[12] W. L. Morrison in the Foundry, 1922, page 33.

burned iron that he has observed. The evidences of oxidation were too strong and efficacy of deoxidizing measures as a cure were too pronounced, to make readily tenable any speculation that chemically reducing conditions were at the root of the trouble experienced with the iron. However the possibility of the reaction taking place even infrequently is worth investigation, as also is the one concerning the absorption of calcium by iron in the electric furnace.

The oxygen question of cast iron is bound to remain unsettled as far as universal conviction is concerned, until analytical chemistry rises to the occasion. At present there is no generally accepted adequate method for determining all the oxygen in iron or steel. The Ledebur method is practiced here and there, but admittedly has serious limitations, it being claimed that it reaches at best only seventy-five percent of the ferrous oxide that may be present,[13] while it misses entirely the oxides of manganese, silicon and titanium. Few contributions to metallurgy could at present be greater than a complete set of accurate practicable methods for determining oxygen and oxides in the various metals and alloys. Let those analytical chemists who feel that dull and futureless is their lot ponder this opportunity for making a well nigh monumental contribution to practical metallurgy! In the same category we may also include nitrogen and other gaseous elements. The arc electric furnace, particularly the long-arc furnace, with its seeming possibilities for nitrogen fixation, makes pertinent the question of determining nitrogen readily and studying its effects upon iron and steel. There are the Allen method, and one or two others, for determining nitrogen but they are attended by an uncertainty similar to that of the Ledebur oxygen method.[14]

We are forced to admit that chemical analyses as now made of metals and alloys often are only part analyses, and the elements that are eluding the analyst may be of paramount practical importance.

In no other furnace can superheating be so effectively done as

[13] Bureau of Standards Scientific Paper No. 346, by Cain and Pettijohn.

[14] Very recently (Chemical and Metallurgical Engineering, 1922, **26**, 218) there was published an iodide-iodate method by Hurum and Fay, that may be one of the needed long steps forward in the determination of nitrogen in steel; so far no mention has been made of its applicability to cast iron.

in the electric furnace. Either the acid or the basic furnace is a good superheater, but the former has some disadvantage in that too high superheat, sometimes (depending considerably upon the quality of the refractories) has a tendency to raise the silicon unduly. Several times the writer has seen as high as 3.80 percent silicon in cast iron coming from an acid furnace that went in at barely 2.00 percent. In the basic furnace the tendency is toward a slight reduction.

The advantages of superheating can all be summed up in the one word "fluidity." The electric furnace gives fluidity to irons not commonly considered fluid, a conspicuous example of which is low-phosphorus iron. This class of irons generally is pre-eminently strong, but unsuited for castings needing fluidity. Superheating in the electric furnace can make many of these irons eligible for the thinnest of sections.

Fluidity is a strong assurance of solid castings through freedom from blow holes, shrink holes, slag inclusions, and the like. Superheated metal increases the effectiveness of risers by lengthening the period of fluidity which is their only period of activity as feeders, and thereby obviates to a large degree that internal shrinkage that comes from fluid contraction of the metal. Abetted by super-hot metal the efficiency of the ordinary riser becomes surprising.

Blow holes seem to be eliminated to a considerable extent by superheated metal acting through risers. The ferrostatic pressure of molten iron is nearly one-quarter of a pound per square inch for each inch of head. In any mould of ordinary dimensions this is not great enough to increase perceptibly the density of the metal itself, but it seems sufficient to prevent the release of dissolved gases from the metal and the consequent formation of blow holes. In this way the pressure of fluid molten metal may be said to increase the actual density of the castings themselves by the elimination of blow holes. This tendency of very fluid iron to prevent by pressure the liberation of dissolved gases perhaps is somewhat unnecessary in the cases of electric furnace irons that have been through sufficient refining to insure practical degasification.

In connection with the gases CO and CO_2 held by the metal in solution or otherwise, there was a significant paper read before the Iron and Steel Institute (British) in the autumn of 1920,[15] by Honda and Murakami, in which it was claimed that in pure iron-carbon alloys graphite is formed not as the direct result of the decomposition of cementite at high temperature according to the reaction, $Fe_3C = 3Fe + C$, but rather through the catalytic action of CO or CO_2. Should this hold true with impure alloys such as cast iron, the removal of these gases in the electric furnace might be expected to have a retarding effect upon the precipitation of graphite.

The present writer has seen some evidence to strengthen this theory, chief of which is an occasionally apparent capability of electric-furnace cast iron to carry higher silicon without perceptible opening of the grain, excessive graphitization and the consequent softening and loss of strength, than a similar iron is capable of that has not been refined. In other words degasification in so far as the elimination of CO and CO_2 are concerned may explain a part of the increased strength and soundness of electric furnace cast iron, on the ground of its ability to discourage a headlong massive precipitation of graphite. It may be that this retarding influence modifies the form of the graphite as well as influencing finer and more advantageously dispersed particles. This is far from a settled matter and the main object in introducing the idea is to stimulate thought and perhaps point out a path for investigators to explore.

To conclude, it may be that the electric furnace never will acquire the widespread use for cast iron that its most enthusiastic friends predict and desire, yet the writer of this paper does not feel that its usefulness to the art of iron founding is to be measured solely by its number of installations. If it accomplishes nothing more than to inspire a new and fruitful interest in the many problems of cast iron it may well be said to have been a generous benefactor to all branches of the art. Not only does the electric furnace open up new avenues for the production of cast iron but also new lines for thought and experiment, and who is the man to declare that this last is least in importance?

[15] Also see Chemical and Metallurgical Engineering 1922, 26, 180.

DISCUSSION.

Richard Moldenke[1]: While visiting Krupp's last year, and during an evening with their Chairman of the Board, Dr. Otto Wiedfeldt, now Ambassador to the U. S., I took occasion to inquire into the methods by which they got excellent gun forgings from steels of very indifferent compositions. It was found to come entirely from a most careful adjustment of the various processes on a scientific basis—which allowed a much wider range of end compositions than was thought possible, until actually worked out.

I am much interested in the things Mr. Elliott brings out in his paper. What occurs in steel, however, must not be applied to cast iron without serious discrimination. For instance, the question of pouring temperature in cast iron makes a big difference in the condition of the carbon in the casting. Then, again, cast iron is so un-homogeneous in structure, even in its best condition, that it is difficult to judge the relative effect of variations in composition, temperature, section, etc., with any degree of certainty.

The sulphur situation in the country since the war is very bad indeed. I have recently seen records of daily runs in which the sulphur varied from 0.21 to 0.26. This is bound to get even worse when the castings made during the war find their way into the scrap pile in regular course.

Mr. Elliott is right in asking for more dynamic tests on our iron to show up the real quality of the metal. Undoubtedly sulphur has a real influence that must be reckoned with, even if considerable may be present without apparent deleterious results. Thus, a cast iron pipe may stand up all right under the ordinary physical tests; but subject it to water-hammer, and high sulphur will quickly cause failure. Hence the advisability of encouraging electric furnace cast iron as much as possible, as this can be made very free from sulphur.

The following memorandum on duplexing cast iron in Germany will be of interest in connection with the discussion of electric furnace cast iron.

Works Manager Koella, in conjunction with Dr. H. Nathusius,

[1] Consulting Metallurgist, Watchung, N. J.

made their first refining tests in the electric furnace of molten cast iron from the cupola in 1918, and the tests turned out so well that the entire production of gray iron castings at the Vogtlaendische Maschienenfabrik in Plauen is now duplexed, and no cupola iron poured into molds direct.

The usual day's run consists of four charges of five tons each run during an eight hour day. Occasionally five charges are put through, in which case, however, the sulphur content of all the heats suffers considerably as the time of refining in the electric furnace is cut correspondingly short. Nothing but scrap is melted in the cupola, 20 percent of which consists of steel. No additions are made to the metal in the cupola or big crane ladle and the entire charge is tilted into the electric furnace hearth. Here the necessary lime and fine coke additions are provided and the reactions go on for 40 to 60 minutes. The first charge necessarily takes a little longer in spite of the pre-heating of the electric furnace. After testing the metal for temperature with the usual spoon ladle by pouring into an open sand mold and rabbling in the required ferro-silicon and ferromanganese, the entire charge of iron and slag is tapped into the pouring ladle. The slag is removed with particular care, for at the existing temperature this is very thin and apt to enter the molds with the metal. The composition of the iron before and after duplexing is about as follows:

	Cupola Iron	Electric Furnace Iron
Total Carbon	3.35	3.00
Silicon	1.60 to 1.70	2.00 to 2.30
Manganese	0.35	0.55
Phosphorus	0.06	0.06
Sulphur	0.23	0.05

The exceptionally low phosphorus for foundry iron will be surprising to American foundrymen, and is evidently due to the German ore situation. The sulphur, however, is disagreeably familiar. The increase in silicon and manganese comes from the ferro-additions. On occasions when it was impossible to tap promptly to make use of the molten metal, the sulphur content actually went down to 0.01, which shows what can be accomplished if time and added cost need not be considered particularly.

Improvement in the quality of the castings was noticed at once. Pin holes, excessive shrinkage, hard spots and other troubles

traceable to cupola oxidation, disappeared and the wear and tear on the machine tools has been reduced. The iron made is tough but not hard. The strength of the castings has risen 30 to 40 percent, and was readily pushed up to 100 percent when occasion demanded it. The greatest advantage, however, was found in the reduction of the percentage of defective castings made, particularly in automobile cylinders. Naturally, the refractory qualities of sand and cores had to be raised to care for the higher temperatures involved.

A very complete table of costs is given by the "Giesserei-Zeitung," which is interesting only in the subdivisions enumerated, as the figures themselves are based upon conditions entirely different from those existing in America. Such items as coke for pre-heating the electric furnace, magnetite and core-binders used in the operation are not often given, and the depreciation is set at the rather high figure of 20 percent, with interest on the investment at 5 percent. The cost calculations for German conditions, with an allowance of 7 percent for melting loss in the cupola and 3 percent in the electric furnace, brings out the molten metal about 30 percent cheaper than the corresponding grade could be made by melting in the cupola only. This would come from starting with an all-scrap charge as against the usual pig and scrap mixtures.

The current consumption will be of interest. The Kw.H. in the eight hours for the charges from No. 1 to No. 5, where five heats were duplexed, ran as follows: 340, 240, 190, 150 and 140. The current consumption with the last two charges became rather constant, and hence it is judged that by continuing operations for a longer period the average current consumption could be cut to 160 to 170 Kw.H. per ton of molten metal ready to pour.

The advantages of the duplexing method are summed up as follows by the officials at the Plauen plant:

(1) Lower cost of molten metal than obtainable in cupola melting process.
(2) Ability to make better cast iron than is possible in the cupola.
(3) Smaller percentage of defective castings.
(4) Machining costs lower, for tools.
(5) Machine labor costs lower by reason of performing work on fewer castings turning out defective. Piece-work rates can be lower as castings are not hard.

(6) Better sales opportunities at higher prices for quality work produced.
(7) Ability to use borings and turnings.
(8) Easier regulation of composition and temperature of end result.
(9) Pouring facilities better, particularly in small castings shops. No waiting of gangs of molders at the cupola spout for molten iron.

Production cost of one ton (metric) of cast iron by duplexing in cupola and electric furnace, based upon an average consumption of 220 Kw.H. per ton at a cost of 0.65 mark per Kw.H. with scrap at 650 marks per metric ton, is indicated below.

Allowance is made for 7 percent melting loss in the cupola and 3 percent in the electric furnace. Hence about 1,000 kilograms to give a ton molten metal.

	Marks
1,100 kg. Scrap @ 0.65 mark	715.00
Cupola Melting Costs	196.00
Current in Electric Furnace (1.03 x 220 x 0.60)	136.00
Ferromanganese	30.00
Ferrosilicon	32.00
Electrodes	5.00
Coke for pre-heating furnace	8.00
Lime	7.50
Dolomite	1.25
Other fluxes for slag-making	5.25
Magnetite and binders	2.75
Wages for electric furnace operation	19.50
Wages for repair gang and materials	22.00
Miscellaneous operating costs	7.00
Depreciation (20%)	15.00
Interest on investment (5%)	8.00
Total for 1,000 kg. (1 metric ton)	1,210.25
Deducting from this total, value of 30 percent sprues at scrap rates (300 x 0.65)	195.25
Cost of 700 kg. castings, would cost (metal only)	1,015.00
Or one ton of castings (metal only)	1,450.00

German conditions have it that a ton of molten iron in castings, when made by the cupola process only, would cost about 400 to 500 marks more than duplexed metal. (Cupola requires pig and scrap mixtures).

In connection with the desulphurization of cast iron in the ladle, I might mention what I saw in Germany last year. The usual methods now pursued are either to increase the content of pig iron in mixtures, and thus dilute the sulphur content of the

result; or to use the basic hearth electric furnace for a straight desulphurization.

The third method, as I saw it, was to apply a chemical upon the surface of a ladle of molten iron, and within two or five minutes remove about 40 percent of the sulphur content, by absorption in the slag made. If the temperature of the metal is still high enough to repeat the treatment, another 40 percent of what remains may be taken out, and say a 0.14 sulphur metal brought down to one with 0.045, or thereabouts. This new method—using likely a potash compound for the purpose—is coming over to this country shortly, and will doubtless prove a blessing to the small foundryman unable to invest in the electric furnace.

G. K. Elliott: In Dr. Moldenke's discussion there is much interesting material, and relative to running a number of duplexed heats per day in the German foundry I should like to inquire how in this foundry the electric furnace and the cupola were synchronized. This is one of the problems of duplexing. One solution is to use the excess cupola melt for lower grades of castings; but, judging from the poor quality of the raw material melted in the cupola in this German foundry I should say that the unrefined iron would hardly be fit for direct casting. The other solution is to hold the cupola with blast off for the necessary time between electric furnace charges. In the table of analyses given by Dr. Moldenke I am struck by the fact that the silicon of the electric furnace iron is markedly higher than in the cupola iron, which tends slightly to bear out an observation I have made that basic electric furnace iron will stand more silicon than cupola iron without opening up the grain. My experience also leads me to emphasize Dr. Moldenke's statement that the greatest advantage of the process lies in the reduction of the number of defective castings. Test bar results are mildly interesting but defective castings reports are convincing. I should like to have Dr. Moldenke tell us how the German foundry preheats the electric furnace.

Referring to the sulphur question I should like to add one more to the list of reactions that may affect this element. Although I have not had the opportunity to test it out very thoroughly it seems to me that even in the acid electric furnace there may occur reduction of sulphur through what perhaps our ore treaters

might call the "flotation" of a part of the manganese sulphide. I do know that irons fairly high in sulphur and manganese while standing in the very large mixing ladles frequently lose as much as one fourth of their sulphur by this simple action, and it seems entirely logical to predict the same action in an electric furnace. However it should not be forgotten that sulphur and manganese both must be high for this reaction to show to a noticeable degree.

RICHARD MOLDENKE: Mr. Elliott is perfectly correct in regard to the undesirability of running alternate mixtures of good metal and scrap, as I have just proved this out in a series of tests made for the Bethlehem Steel Company with nickel-chrome pig iron. When putting a series of mixtures into the cupola, each differing from the other, and yet placing double coke charges between them to help melt them separately, they would persist in running together so seriously that this has formed the subject matter of a special paper given before the foundrymen's association, as of importance in connection with their daily routine.

A further point might be the cupola installation. Here we use a few very large capacity cupolas in our great foundries. In Europe they use a large number of small diameter cupolas at the same time, and hence can get several classes of metal without running more than one mixture in each cupola. One often sees a dozen cupolas 36 inches diameter in a European foundry, where we would have two or three here of 54 inches to 84 inches diameter. The European practice is better for the resulting work, though more costly in operation.

A third way would be to operate a cupola intermittently. Melting an hour or so, then stopping completely, and resuming again. This is readily accomplished, for when the blast is shut off, melting ceases. If care is taken to drain the cupola completely, no trouble is experienced in starting up again. If the stop is premeditated, it is well to previously introduce extra coke so that when stopped, the cupola may be with an extra high bed for the time, and thus may lose some coke while standing without getting the bed too low.

BRADLEY STOUGHTON[2]: It seems to me that a word should be put on record regarding this question of high sulphur in iron. It

[2] Consulting Engineer, New York City.

is very much like Banquo's ghost, it will not be settled; although dead it comes up again at intervals. If you look up the literature previous to 1850, you will find that the point was brought up, actively discussed, settled once for all and it was definitely proved that high sulphur is a bad thing for iron and steel. Then if you look up the literature between 1850 and 1875, you will find repetition; again between 1875 and 1900; 1900 to 1922, and we are about due for another resurrection of this subject. So we might just as well put it on record that that question has been settled and it is settled every time it comes up, but it keeps on coming up.

R. J. Anderson[3]: There is one thing that occurs to me in connection with these general papers; I think it is alluded to in Mr. Elliott's paper as well as in others that have appeared in the literature, viz., that casting losses may be lower in the case of cast iron poured from the electric furnace than from the cupola, and I would like to ask if there are any figures available to show this.

G. K. Elliott: I do not have the actual cost figures but I do know that, in spite of the fact that the electric furnace iron in the ladle costs more than the cupola iron, the finished castings cost less because of the great reduction in the number of rejections. It was this and the general superiority of the castings that made the duplexing process a commercial success in our plant.

R. J. Anderson: What I mean to say is, were your foundry rejections lower?

G. K. Elliott: The foundry and the machine shop rejections both were reduced and the process was adopted because practically all the castings it produced were able to pass the final tests and inspection.

Robert J. Young[4] (*Communicated*): The use of the electric furnace for melting cast iron is, as we know, in its infancy, and much experimenting must be done, before it attains to its highest state of efficiency, so that it may compete with the cupola.

Much has been said regarding the make-up of charge, and the manner in which it is charged, so as to get better conductivity, thereby cutting down the length of time per heat. It has been my

[3] Metallurgist, Department of Interior, Bureau of Mines, Experiment Station, Pittsburgh, Pa.

[4] In charge of electric furnace, Philadelphia Navy Yard.

experience that it does not make much difference whether you have all large pieces of scrap and pig iron or a mixture of large and small or a hot or cold furnace to start with, you will still have the trouble of no conductivity at the start. I have tried various methods to combat this difficulty. The mixing of iron borings with the scrap and the addition of steel turnings to the charge both in it and around the electrodes brings no improvement, but rather tends to give more trouble in that the borings seem to work themselves to the bottom of the furnace where they form in a compact mass, not melting without the rather difficult and mean task of prying them loose with a bar or rod several times during the heat. The best method I have found is to mix in the charge at various places the burned up stirring rods, etc., that accumulate around the furnace, making an effort to place them so that they join the electrodes in a delta in the case of a Héroult furnace or straight across in the case of a Greaves-Etchells such as I am operating. The only advantage (and a big one) of a hot furnace over a cold one to start with is that it saves the price of approximately 200 Kw.H. per ton. This is also true in the case of steel making.

I have found it desirable as soon as you have good conductivity, to make the lime additions, assuming we are working a basic furnace, follow with the fluorspar and carbon, to form the deoxidizing slag for the removal of the sulphur, and to maintain this reducing atmosphere throughout the entire heat, thereby lengthening the time of the action of the carbide slag on the metal, thus giving a lower sulphur content and liberating more of the gases detrimental to a good product. The addition of manganese to the bath as soon as permissible is also a helping factor. Following closely the percentage of sulphur in the bath just before tapping and just after the metal is in the ladle, I find that considerable sulphur is liberated if the slag is permitted to run into the ladle with the metal.

The proportion of iron scrap to pig does not seem to affect the ultimate product. The various proportions seem to produce the same grain size and closeness of metal and the physical properties seem to remain about the same, as Table A would indicate. The iron scrap used in the heats of this table was not carefully selected,

TABLE A.

Heat No.	Charge (in percent)			Analysis							Kw.H. Per Ton	Hot or Cold Furnace	Remarks
	Iron	Iron Scrap	Steel	Total C	Combined C	Graphitic C	Mn	P	S	Si			
248	60	20	20	2.56	1.30	1.26	0.62	0.021	0.016	1.18	. . .	Hot	Could not machine.
576-A	40	50	10	2.80	0.55	2.25	1.22	0.51	0.020	1.66	877	Cold	Machined hard on outer surface or skin.
585-A	91	..	9	3.25	0.92	2.33	1.02	0.53	0.014	1.72	840	Cold	Machined O. K.
590-A	91	..	9	3.07	0.07	3.00	0.76	0.53	0.015	2.01	684	Hot	Machined O. K. 0.50 Nickel added
594-A	50	50	..	3.37	0.92	2.45	0.75	0.49	0.028	1.63	604	Hot	Machined O. K. 1.00 Nickel added.
596-A	50	50	..	3.48	0.58	2.90	0.97	0.46	0.038	1.60	615	Hot	Machined O. K.
599-A	20	80	..	3.29	0.36	2.92	0.98	0.54	0.048	1.63	596	Hot	Machined O. K.
600-A	16	84	..	2.80	0.70	2.10	0.99	0.52	0.025	2.02	946	Cold	Ore and mill scale added to charge; had to add FeSi; machined O. K.
601-A	50	50	..	3.11	0.39	2.72	0.97	0.51	0.036	1.44	887	Cold	Machined O. K.

Physical Results

Heat No.	Tensile as Cast	Tensile Heat Treated	Transverse as Cast	Same Heat Treated
576-A	21000	.....	3150	
585-A	28409	31500	3185	3200
590-A	25000	.....	2450	
594-A	.....	28400	.....	2780
596-A	33650	35385	3560	3830
599-A	31772	.....	3470	
600-A	30000	.....	3100	
601-A	31300	.....	3250	

only that we tried not to get any semi-steel in it, otherwise we took it as it came from the pile, including grate bars, flash bars, etc. Contrary to expectations the additions of steel scrap gave us lower physical results. From heat 600-A we poured a small bushing 4 inches in diameter, had it machined inside and out, leaving only a ⅜-inch wall. On this we put a water pressure of 750 lb. without a sign of a weep or leak. We could not hold the gaskets at a higher pressure so we had to stop.

The absence of the usual pin holes on the top surface of an open sand casting is very noticeable and the surface of other castings seems to be much better.

I have experimented with the pouring of iron through the bottom of the ladle with surprising results, using the ordinary steel ladle with a two-inch nozzle. You get a more uniform pressure, and have complete control of the stream throughout the heat. It eliminates the going back and forth to the furnace for more hot metal, the slag on the surface of the ladle helps to retain the heat, and the teaming time is shortened considerably. It saves the wear and tear on the furnace lining, by not lowering the slag line and reduces the chances of losing the silicon or manganese of the bath as well as saving Kw.H. consumption.*

The class of work poured with this metal has a wide range going from fingers for automatic stokers to turbine housings, including very difficult designs and sections for ship work. It is however mostly used for Diesel engine work, cylinders, etc., required to stand high pressure steam and water.

The effect of the iron heat on the following steel heat, as indicated in Table B seems to be on the carbon, and it usually does not make its appearance until the heat is nearly ready to be tapped. To off-set this condition, it is very necessary to go ahead on a lower carbon than the requirements call for, or to make a further call upon the laboratory for a check on the carbon. This indicates that the carbon does not go into solution until the furnace has almost reached its maximum temperature.

The cost of electric iron as I have found it and comparing it with cupola melting is slightly greater than the latter or a

* In this method of pouring there must of course be a change from the usual way of making gates and runner boxes, so that the metal does not cut or wash away the sand from around same. The usual large basin at or around the gate can also be eliminated, thereby saving metal.

TABLE B.

Steel Heats Following Iron Heats

Heat No.	Class	C	Mn	P	S	Si	Ore Added
249	B	0.27	0.46	0.019	0.03	0.37	350*
277	B	0.24	0.42	0.03	0.038	0.32	None*
586	A	0.40	0.63	0.023	0.026	0.23	350*
591	B	0.35	0.69	0.053	0.027	0.37	300†
595	B	0.42	0.75	0.023	0.025	0.29	None†
597	B	0.50	0.99	0.038	0.024	0.37	None‡
600	B	0.31	0.67	0.046	0.027	0.34	None†
601	B	0.28	0.67	0.025	0.042	0.33	None†

* Slagged twice
† Slagged one time
‡ This was after two successive iron heats.

fraction of a cent more, which is off-set by a much better product and a considerably smaller scrap pile, which means a lessened eyesore to any well regulated foundry.

The thinnest section poured was 3/16 of an inch. This was a motor frame casting about 4 feet inside diameter and about 3 feet 6 inches long, cast in halves.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, Vice President Hinckley in the Chair.

SYNTHETIC CAST IRON.[1]

By Jas. L. Cawthon, Jr.[2]

The name "synthetic cast iron" is one of the many war legacies. Two of the developments of the frenzied production necessitated by the stress of those times were an acute shortage of pig iron, and the production of an enormous amount of scrap from machine shops in very light sections, borings, turnings, etc. These grades of scrap materials, be they of ever so splendid a chemical analysis, were not proper material for cupola or open hearth charges. The steel turnings oxidize too highly in the open hearth, owing to their great amount of exposed surface, and the borings do the same in cupolas and, in addition, are blown out. A rather large amount of ferrous metal raw material for the open hearth and cupola was consequently ruled out by its own shortcomings; or perhaps, more aptly, by the characteristics of the melting mediums. While the electric steel manufacturers were utilizing a certain percentage of the supply of turnings, the iron foundries were practically dependent on the supply of pig iron and good scrap available, and their difficulties were accentuated by the poor grade of foundry coke then available.

In several outstanding instances, advantage was taken of the electric furnace, which possessed the necessary metallurgical flexibility to melt these materials, and make such adjustments in their analysis as were necessary. Excellent results were obtained in several instances, and the cast iron thus produced was given the name of synthetic cast iron.

The practice by no means became general, or even extensive, the economic feasibility depending on many things, chiefly power cost and availability in large quantities. Outstanding examples were the production of shells by the Keller works at Livet,

[1] Manuscript received April 4, 1922.

[2] Pittsburgh Electric Furnace Corp., Pittsburgh, Pa.

France, washed metal by the Anniston Steel Company at Anniston, Alabama, and steam pipe fittings in Portland, Oregon. The first named company produced several hundred thousand tons of synthetic cast iron shell castings for the French ordnance department.

The reduced condition of general production has so lowered the demand and cost of pig iron, that at the present time practically no synthetic pig iron is being made, except an occasional experiment. It may be said, too, that a lack of experience and general understanding of the adaptability of the electric furnace for this work, prevented wider use during war time.

The term "synthetic cast iron" is rather a broad one, a synthesis usually inferring the compounding of a definite substance from its component elements and compounds. "Cast iron" is not itself a very determinate classification, and for the purpose of confining this paper to its proper limits, only those ferrous alloys containing from 2.25 to 4.00 percent of carbon, with varying percentages of Mn, Si, S and P are discussed. Several grades of material have been produced, among which are washed metal and low phosphorus pig.

The production of synthetic cast iron consists of melting steel scrap, or combinations of iron and steel scrap, in the acid or basic electric furnace, with a highly carbonaceous material (coke, oil still residue, or coal) to give the necessary carbon content to the iron, and making adjustments in the percentages of manganese, silicon, sulphur and phosphorus, to give the desired characteristics in the finished metal. The process is fairly simple in its chemical aspects, though a certain amount of experience and judgment is necessary if the results are to be satisfactory from an economic and physical standpoint. For the purpose of encountering some of the problems, the average conditions and history of a heat will be related.

An iron, say, of the following specifications is to be prepared: C, 3.25; Mn, 0.70; P, 0.50 or under; S, under 0.07; Si, 1.90 to 2.10. This would be an ordinary soft grey iron. The material available for charging is steel turnings of the following analysis: C, 0.20 to 0.30; Si, 0.25; S, 0.05; Mn, 0.60; P, 0.05. A basic furnace is to be discussed first, followed by acid condition.

The charge per ton for this heat will be made up, for the basic heat, as follows: 2000 lb. turnings; 75 lb. coke (coal or oil still residue); 20 to 30 lb. lime (preferably under 3 percent MgO). The charging is done so that the coke and lime are mixed with the first third of the charge going on the bottom of the furnace.

The power being on, nothing can be done until the charge is about two-thirds melted, at which time several shovels of a mixture of two parts coke breeze and five parts lime may be added. On melting down, the bath will be covered with a carbide or falling slag, and will have as an average figure the following analysis:

	Percent
C	2.40 to 2.60
S	0.025 to 0.035
Si	Practically nil
P	0.05
Mn	0.65 to 0.68

It will be a well deoxidized metal and, except for discrepancies in analysis and probably temperature, quite ready to pour, being about 0.75 percent low in carbon and 2.00 percent low in silicon. It is satisfactory in all other respects with the possible exception of the phosphorus.

For an acid furnace, the charge would be exactly the same as for the basic heat, excepting that no lime would be included. Supposing that this heat had been melted in an acid furnace, the analysis of the bath after being brought to a molten condition would be as follows:

	Percent
C	2.40 to 2.60
Si	0.20 to 0.40
S	0.05
P	0.05
Mn	0.35

Not much change has taken place in the S or P, while the carbon is the same as in the basic heat. About fifty percent of the manganese has gone into the slag, while a small percentage of silicon has been reduced from the slag. In the acid heat, it is necessary to add 0.35 percent Mn, 0.75 percent C, and 1.60 percent Si.

The comparison between the two types of operation has been drawn for the purpose of contrasting the acid and the basic methods, the data being average figures obtained on a number of heats made in both ways. The conditions of the bath in each case are those which would automatically and regularly take place under normal circumstances.

The adjustment of the analysis for each element is carried out as follows:

Carbon—In melting steel scrap under recarbonizing conditions, such as described above, the author has found that it is almost inevitably the case, whether the conditions be basic or acid, that the heat will melt down with a carbon content of 2.50 to 2.75 percent even though a much greater excess of carbon than that given in the charge be introduced into the furnace during the melting operation. The raising of the carbon percentage above that point takes a certain amount of time and a very hot bath. The absorption of carbon by iron is proportional directly to the time of contact between iron and carbonizing agent, intimacy of contact, and temperature of the iron, and of course, progresses more slowly as the absorption approaches saturation.

With a good excess of highly carbonaceous material floating on the bath, carbon above 2.5 percent is picked up very slowly, even though the temperature be high. This is probably due to the fact that as the carbon content of iron increases the specific gravity decreases, so that the portions of the bath in contact with the carbonizing material become highly saturated with carbon and tend to remain on top, thus insulating the more poorly carbonized portions of the bath from the carbonizing agent. This tendency is also accentuated by the fact that, in contrast with steel in the electric furnace, cast iron does not boil or circulate to a marked degree.

The author has tried various expedients to accelerate this carbon pick-up, and has found that agitation of the bath is the one on which main reliance can be placed. The bath is gotten to a high temperature, slagged bare and clean. About fifty to seventy-five pounds of coke per ton of charge are then thrown over the bath. The doors are closed to allow the coke to become incandescent. A green pole is then introduced into the bath which is

vigorously stirred. The gases distilled from the wood boil the metal violently. One-half percent of carbon can thus be picked up in about five to ten minutes. It is quite frequently necessary to repeat this operation twice, particularly if carbon contents well over 3.00 percent are desired.

During this operation a considerable amount of gas is dissolved in the iron, so that sufficient time to allow this to escape should be given the heat before tapping. From the author's experience, the only method of securing carbon contents well over 2.75 percent is to use a combination of very hot metal, a clean bath, and vigorous agitation for a fairly well sustained period.

Silicon—The adjustment of the silicon content is a simple matter. The addition is made in the form of 50 percent ferro-silicon. In the basic furnace, the silicon addition should always be made at the very last of the heat, to secure the maximum absorption and minimum loss to the highly basic slag.

In the acid way, a percentage of silicon may be reduced from the slag. Under certain conditions, if the temperature is allowed to get high, the slag highly acid, and the furnace condition highly reducing, a considerable amount of silicon will be reduced from the slag. The action which produces this takes place at a very rapid rate, conditions being propitious, and closer analysis may be obtained if this condition be avoided, relying entirely upon ferro-silicon addition.

All three of the conditions mentioned above are necessary to silicon reduction, and by modifying any one of them it can be stopped instantaneously. The simplest method is to introduce a small amount of fire clay or lime immediately under the electrodes. To the operator experienced in acid electric furnace operation, the condition is immediately apparent by several signs, among them being the almost total silence of the arcs, the extreme paucity of fumes around the electrodes, and the general "tightness" of the furnace.

It may be added here, that this condition which comes about in the acid electric furnace is indicative of a highly deoxidized condition of the bath. Tests taken from heats under this furnace condition show the metal to be in excellent condition. Its use, with proper judgment and understanding, may therefore well be

adopted. Some steel foundries regularly allow a heat to come to this condition incipiently before tapping, the results being reflected in the soundness of the castings.

Manganese—In melting steel scrap the basic way, practically all of the manganese is retained in the metal throughout the heat. In the hypothetical instance given, no adjustment of the manganese content is necessary. This is a highly advantageous feature of basic method, except in instances where an exceptionally soft metal is desired. The heat can, of course, be melted first under slightly oxidizing conditions and slagged off, but this method is to be avoided, as it consumes labor, power and slagging material. But for ordinary grey iron production, this is no objection and contrarily a decided advantage.

If an increment of manganese be necessary it can be added at any time, even included in the charge. Perfect absorption efficiency can be expected. The manganese will do most good if thrown into the bath immediately after the recarbonization is complete, being a decided help in degassifying the heat.

In the acid heat, it was noted that about fifty percent of the manganese was lost, being absorbed in the slag as a silicate, $MnSiO_3$. This manganese is not recoverable to any extent and to all purposes may be considered lost. The addition of ferro manganese to an acid heat should be made just before the heat is tapped, and before doing so, the silicon addition should have been made.

By controlling the acidity of the slag and keeping it to about 60 percent acid, the efficiency of manganese absorption to 85 percent is possible. It is, of course, feasible to make the manganese addition to the ladle, a practice which is favorably considered in many foundries using acid practice on steel. The same considerations hold good in iron. In the practice of increasing manganese content by ladle additions, practically 100 percent absorption results in grey iron.

The author wishes to say that, provided the manganese in synthetic or electric furnace grey iron be sufficiently high to more than fulfill the dictates of the sulphur-manganese proportion, the further addition of manganese does not seem to have a decided

effect on the physical characteristics of the metal, particularly with carbon contents of 3.25 percent or over. With carbon under 3.00 percent the hardening and strengthening effect is notable.

Sulphur—The marked sulphur reducing action of the basic electric furnace has been thoroughly discussed in papers read before this and other societies, so that no time should be taken to dwell upon it here. It is noted in the anlaysis above given that a marked elimination of sulphur takes place. With the formation of the slag after the recarbonizing is complete, this sulphur reduction will continue. It is pointed out, though, that if coal, or a high sulphur carbonizing agent be used, a material increase in sulphur may occur. This, however, will be eliminated by the carbide slag formed before the metal is tapped, and is not a matter with which to be much concerned.

In the acid way, no decided reduction of sulphur is practicable. The only precaution which can be taken is to make certain that the sulphur is balanced by the necessary amount of manganese. Two to three times the theoretical amount necessary to absorb the sulphur as MnS is sufficient. One foundry making electric grey iron castings in the acid way, reports an inherent reduction of about 0.01 percent S on each melting. This is no doubt due to the action of manganese. The resulting MnS is absorbed in the slag. There is no sufficiently stabilized practice as yet to justify depending on this as a means of meeting rigid sulphur specifications.

With respect to sulphur limitations as a feature of synthetic cast iron, it is hardly necessary to give a great deal of attention to the matter if steel scrap be contemplated as the base. The great majority of pig iron melted is well over 0.07 percent in sulphur and, in the absence of any pick-up in the sulphur content with electric melting, the demand for 0.05 percent in castings can be met by melting steel scrap of the proper S content, which will undoubtedly be available for some time to come. Sulphur reduction as a means of gauging the state of deoxidization is a valuable asset in basic melting of grey iron or in duplexing cupola metal. At least under present conditions, in the synthesis of grey iron from steel scrap, it is believed by the author to be a matter of relative unimportance, at least from an economic standpoint.

Phosphorus—Referring once more to the hypothetical analyses applying to the chemistry of the heat after melting is complete, it will be seen that in neither case, acid or basic, is there any great change in the phosphorus content. Phosphorus is rapidly eliminated from iron only under highly oxidizing and strongly basic conditions, at comparatively low temperatures, and not to any marked degree with carbon contents very high. It will thus be seen that with furnace conditions recarbonizing and reducing there is no great opportunity of phosphorus reduction in the basic or acid heat. In either case it will remain constant, finishing with the amount present at the start.

Since the only advantageous function of phosphorus in cast iron is fluidity and that asset is obtained in the electric furnace by a temperature increase, the phosphorus can be materially reduced in synthetic grey iron, thus refining grain structure and reducing brittleness. Due to the increased expense attendant on phosphorus reduction, it should not be contemplated as a furnace operation, even in the event of using percentages of high phosphorus iron, which will be discussed later. If phosphorus must be kept low, it should be accomplished by the expedient of using sufficient quantities of low phosphorus material (steel) in the charge.

For the production of the low phosphorus iron, called washed metal, which usually has a phosphorus specification of under 0.03 percent (and low phosphorus pig) its elimination should be accomplished by using charges made up entirely of steel scrap, and including two large scoop shovels of mill scale or lump ore per ton of steel, in addition to the lime. It must, of course, be carried on in a basic furnace. The carbonizing material should be left out of the charge, and not introduced until the oxidizing slag is removed.

When melting is completed, the bath is raked clean of slag, and is in a wild condition. The carbon and Si content will be low, and the recarbonizing material addition should be figured at 60 percent efficiency of absorption of the contained C. When this is thrown on, due to the formation of carbon oxides, a boil in the bath of such violence occurs that the metal will run out of the doors unless checked, causing a sloppy condition of furnace and floor. The effect of the first shovel of carbonizing material

should be observed, and if the boil starts, two or three pounds of ferro-silicon fines, if thrown into the boil, will immediately cause it to subside. This treatment is usually quite sufficient to prevent any further boil, and the work of recarbonizing can be carried on without further danger from this source.

PRELIMINARY TESTING.

The author has attempted to discuss in detail the manipulation of the heat with respect to its five principal alloys. The matter of testing naturally arises as a question of importance. The best means would, of course, be chemical analysis, but more often than not, the laboratory facilities are not available. Some means of quickly determining the approximate conditions of the bath is necessary. Color carbon tests would be quite satisfactory, but facilities for making even these are usually not available in the average foundry.

The author has devised a quick testing method which was satisfactory for the particular case, using a Brinnell testing machine. A test bar is cast in dry sand core blocks, the bar being 1 inch in diameter and six inches long. The ordinary test spoon holds more than enough metal to pour such a bar. The bar is allowed to stand three minutes in the sand and is then allowed to cool seven minutes in air, and is then quenched and broken. One side of the fracture is ground and Brinnelled. If the metal be found above the hardness desired, the carbon or silicon should be raised by additions. If the metal be found too soft, these elements are lowered by the addition of a certain amount of low carbon steel scrap.

While the Brinnell figure of the test bar is not identical with the figures for the castings poured, since they are usually of much heavier sections, it has been found that there is a consistent relation between the two. By this means, the hardness of the finished castings is controlled to within 10 points plus or minus in Brinnell. After close checking for a few weeks, it was found that the carbon content could be estimated from the fracture with good results.

This method, while not being strictly accurate, is quite certain, simple and decidedly inexpensive and its use is recommended, of course, within its proper limits.

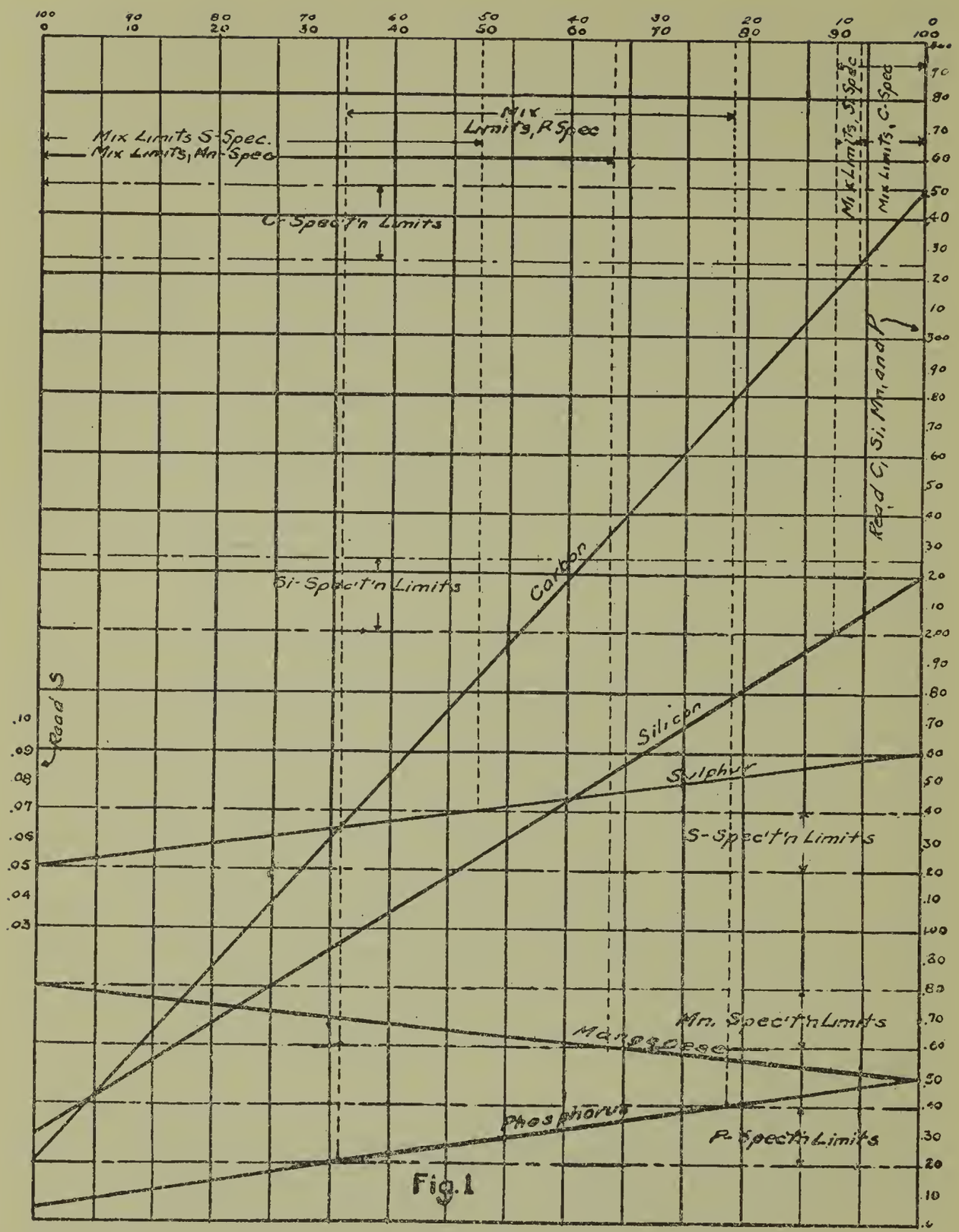


FIG. 1.
Chart for Calculating Charges of Mixed Materials.

MATERIALS.

While the name synthetic cast iron was first applied to the process of making iron from charges consisting of steel scrap entirely, it is highly probable that in this country, at least, the charges will generally consist of mixtures of steel scrap and iron

"borings." Whenever machine shop steel scrap is available, it is more often the case than not, that equal or larger amounts of cast iron borings are also available. The logical course is to use both grades, since they are frequently mixed and are then priced at the same level.

With such mixed charges, no material difference in electric furnace operations is encountered. The calculating of the charge is not quite so simple. The author has used a graphic method for figuring charges which simplifies the calculations and eliminates the major portion of them.

In Fig. 1 such a chart is given. By marking off the analysis of one grade of scrap on one margin, and doing likewise on the opposite margin or zero-hundred percent point for the other material, and then connecting the corresponding element points with straight lines, the resulting analysis of any mixture is immediately seen by projecting a line from the percentage scale at the top of the page to the element line. If horizontal lines be drawn, representing the specification limits for each element, it will at once be seen which mixture percentages will fall without the specifications, and how much refining or adjustment for each element is necessary.

The intersection of the specification limit lines and the element lines can be projected to the percentage scale, each pair of these projection lines then representing the limit of mixture percentages which can be used without getting the resulting analysis for each element outside the specification limits. It is also easy to arrive at the mixture point which requires least analysis adjustment or change, by observing the point within the largest number of these vertical limit lines. This chart is quite simple and has proven handy in quickly figuring large numbers of charges from varying materials.

Local and commercial conditions in their relation to available materials, would constitute a determining factor in proportioning charges. Owing to the high silicon and carbon content of cast iron borings, and the low sulphur and phosphorus content of steel turnings, mixtures of these two materials, utilizing to the maximum the desirable features of each, give the best economic results, and are consequently to be preferred. This refers particularly to malleable, grey or special iron. The production of washed

metal is more economically accomplished by the use of steel alone in the charges, as the decarbonization necessary before phosphorus reduction takes place to the desired extent, consumes too much time and power where cast iron scrap is used.

Highly oxidized materials of any sort are to be avoided. The use of such scrap, while not impossible from a physical or chemical standpoint, will not give efficient or economical production, as the additional time introduced in the heat cycle by the unsettling influence and retarding of carbonization runs costs up and output down.

RELATION OF MATERIALS TO METALLURGY OF THE PROCESS.

As above stated, commercial availability of materials dictates charge composition. The factor of quality and results desired is one of equal or greater importance, and the relative weight of the two considerations must determine the type of electric furnace operation most desirable and feasible.

A comparison of the basic and acid types of operation may be practically summed up in the statement that the basic process provides facilities for reducing sulphur and phosphorus, while the acid process is lower in costs and is simpler in operation, and the slag is much easier to handle in casting from lip pour ladles or shanks. There are some fine points, such as the relative deoxidizing ability of the two processes, and the relative freedom from occluded solid impurities in the two irons, which are more or less mooted questions.

It is not the intention to sponsor either process, but it is the writer's experience that the acid process is more economical and simple in operation than the basic way, while producing metal quite the equal, under like conditions, of the basic. It is believed that the matter of economy is of sufficient weight to make the acid lined furnace preferable, wherever and whenever conditions and specifications of a chemical nature permit. The basic way has great value and, of necessity, must be utilized in those circumstances which dictate its use.

APPLICATIONS.

Synthetic cast iron, while probably not destined to immediate and wide adoption, has certainly a most useful field. It will have

a wide field in localities like the Pacific Coast, which are at great distances from fuel and pig iron supplies and have large quantities of low priced power available. But in this section of the country, its most immediate and logical application will be the production of the castings which require iron of an exceptionally fine grain, great strength, and uniformity of excellent quality. There is certainly a good and growing demand for such castings, and it is only logical to predict that considerable percentages of it will be electric furnace product; and generally speaking, the economies of the synthetic process will dictate its use.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922. Vice President Hinckley in the Chair.

SYNTHETIC AND ELECTRIC PIG IRON SANELY CONSIDERED.[1]

By Robert Turnbull[2]

At the fall meeting of this Society, held in Pittsburgh in 1917, and also at the meeting held in Atlantic City in the fall of 1918, the writer had occasion to present papers covering the manufacture, in the electric furnace, of low phosphorus pig iron from scrap steel turnings. Such iron is now commonly known as synthetic pig iron. It is the purpose of this paper to consider further the manufacture of synthetic pig iron, and pig iron produced electrically from ore, under present day conditions, as well as the possible use of the electric furnace in the foundry, in the manufacture of iron suitable for grey iron castings.

Synthetic pig iron may appear to many to have been born during the late war, to have flourished while the war lasted, and to have died with the war. Little if any such iron is produced today on the American continent, and similar conditions may be said to exist in Europe. It would be a mistake, however, to assert that the last has been heard of synthetic iron, as the present stoppage in its manufacture, is not due to its production being commercially impossible, but rather to the fact that plants engaged in such manufacture during the war, which were specially built to take care of that industry, have been closed down for lack of demand for the product, and also by lack of the necessary raw material.

The writer does not consider however, that synthetic iron will again be produced to any extent in such plants, but rather looks to a more general adoption of the process in foundries where electric furnaces are already installed or could be installed, and where grey iron as well as steel castings are produced, the same furnace serving for both classes of metal. Quite a number of iron foundries, where the electric furnace is in use, have been pro-

[1] Manuscript received March 20, 1922.

[2] Managing Director, U. S. Ferro Alloys Corp., Niagara Falls, N. Y.

ducing grey iron castings from cast iron borings, and with remarkable success, the iron being of a high standard both in regard to strength and machining qualities. So long as these borings can be obtained at attractive low prices, it would not be necessary to look for other raw material.

Unfortunately the demand for cast iron borings is in excess of the supply, mainly due to the large tonnage used in blast furnaces. This source of supply will eventually fail, prices now being paid for such borings, with further advances in prospect, will not permit of their economical use in the electric furnace. However, as iron, suitable for the grey iron foundry, can be produced at about the same cost by the use of steel turnings, as in the case of cast iron borings, synthetic iron may again come back and become a permanent part of the industry.

Both open top smelting type furnaces and steel furnaces have been used in the manufacture of synthetic iron. The open top type is easier to operate, and permits a higher carbon to be obtained in the finished iron, than with the steel furnace. Refining, however, has not the same possibilities in this type as with the steel furnace. The steel furnace is also more adaptable to the foundry, and although carbon over 3.2 percent is hard to obtain, it has been demonstrated that high carbon is not the only essential in the quality of an iron for foundry work. Excellent castings have been made with iron containing not over 3 percent in carbon, the further refining of the metal apparently making up for the lower carbon content.

It is the opinion of the writer, that further study in the manufacture of synthetic iron in the electric steel furnace, especially regarding better methods of carburizing the iron, might result in means being found of producing iron with carbon content similar to what is obtained in the blast furnace. This combined with further refining would make the electric furnace without a rival, where quality metal is essential.

No further advance in the art of producing pig iron from ore, in the electric furnace, has been made if the truth must be told, since the experiments conducted by the Canadian Government at Sault Ste. Marie, Ont., in the winter of 1905-6. It is true that shaft and open type furnaces of considerable size have been built

and are still operating in Sweden, but the results, outside of the fact that pig iron is being produced, are so far from economical that there appears to be little or no future for this industry for years to come. Although at Sault Ste. Marie, it was impossible to estimate correctly many of the costs which would enter into the operation of a large electric furnace plant, some of the items such as power, raw material and slagging materials were correctly gauged. It was proven that with certain ores, a consumption of 2000 Kw. H. per ton was possible, whereas the consumption in Swedish furnaces is in no case less than 2500 Kw. H. If the writer was asked to make a choice between the two types of furnaces, open top and shaft, he would without hesitation be in favor of the former, as the shaft furnace has so far presented no advantages over the other and has considerable disadvantages.

In electric furnace work, hand stoking and the correcting of the position of the electrode in the charge, is more than half the battle, and such work is impossible in the shaft furnace. The charge in this type of furnace, when in the furnace, has to take care of itself. No control can be exercised thereon, with the exception of the preparation of the charge before its introduction into the furnace. One can well imagine what would happen in a ferro-silicon furnace, should it be operated without stoking. There would be a reduction in output of at least 30 percent and considerable variation would occur in the analysis of the alloy produced. There is no reason why the same theory should not be applied to the smelting of iron ore under similar conditions.

Unless improved methods are discovered, which would result in the power input per ton of finished product being materially reduced, which would further result in a proportional decrease in all other items of cost, with the one exception of raw materials, the outlook for expansion in the production of pig iron electrically from ore, is far from promising. The only way open to countries far removed from the source of pig iron supply, is to resort to synthetic iron, by using their available scrap in an open top furnace. In such a furnace by the addition of a very small quantity of carbon to the charge, a first class grade of iron could be produced, which would cover a fairly large percentage of their requirements. Also by mixing a certain percentage of iron ore with

the scrap, if such ore is available, the output in iron could be materially increased.

The smelting of iron ore electrically is a problem that will eventually have to be met, as a day will come when coke will be no longer available, and as it becomes scarcer, an ever increasing cost in this commodity can be expected. With the one exception of Sweden where furnaces are operating, and the experiments by the Canadian Government mentioned above, no serious attempts have been made by Governments or private individuals or corporations, to find improved methods whereby costs of production and power input would be materially reduced. Should such research be undertaken in the future, either by Governments, private individuals or corporations, it is to be hoped that a sane type of furnace will be adopted, and the work be intrusted to men well known in the electrical furnace field. Many of past failures in electric furnace research work may be put down to the work being handled by persons with little knowledge of the practical end of electric furnace work, and to the use of furnaces that were freaks or of impossible design.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, Mr. Bradley Stoughton in the Chair.

A STUDY OF CARBURIZATION IN THE MANUFACTURE OF SYNTHETIC CAST IRON.[1]

By Clyde E. Williams,[2] and C. E. Sims[3]

GENERAL CONSIDERATIONS.

The study described in this paper was undertaken in connection with the sponge iron investigations being conducted at the Northwest Experiment Station of the U. S. Bureau of Mines at Seattle, Washington. Sponge iron is being made by low temperature reduction of iron oxide, and subsequently melted and carburized to produce pig iron. The sponge iron contains about 80 percent metallic iron, 10 percent iron oxide, and 10 percent silica, alumina, and lime. In melting the sponge iron, difficulty was experienced in introducing sufficient carbon into the iron, and, except in a few instances, a product containing over 3 percent carbon could not be obtained. The degree of carburization varied with the different carburizing agents added.

This study of carburization in the manufacture of synthetic cast iron was carried on because of the lack of definite information regarding the factors which influence carburization. Instead of the sponge iron, steel scrap in the form of turnings, punchings, and clippings was used, because it eliminated a number of variables introduced by the impurities in the sponge iron. The results of this investigation consequently have direct bearing upon the present practice of making synthetic cast iron from steel scrap.

Previous investigators have emphasized the difficulty of introducing much more than 3 percent carbon in synthetic cast iron made in the electric furnace, but they have not discussed in detail the relative efficiencies of the different carburizers, the effect of

[1] Published by Permission of the Director, U. S. Bureau of Mines. Manuscript received March 16, 1922.

[2-3] Metallurgist and electrometallurgist respectively, Northwest Experiment Station, U. S. Bureau of Mines, at Seattle, Washington, in cooperation with College of Mines, University of Washington.

impurities, or the various operating details. Turnbull[4] used charcoal, coal or coke, ferro-silicon, lime, steel turnings, and steel scrap, but did not mention the relative advantages of the various forms of carbon employed. He rarely obtained iron whose carbon content was over 3 percent, and then only with much destruction to the furnace lining and roof. Later he[5] apparently improved his practice and was able to get as high as 3.5 percent carbon, seldom obtaining less than 3 percent. Turnbull[5] used, instead of ferro-silicon, "another product which reduces the cost and helps the carbon content." This was evidently silicon carbide. Keller[6] melted steel turnings with carbon that was in approximately the same state of division as the steel turnings. Ordinary coke and wood charcoal, depending on their cost, were used interchangeably. Iron containing 3 percent carbon is mentioned, and an analysis is given of white iron containing 3.55 percent carbon. In discussing Keller's article, Brooke[6] said that it was easy to obtain a carbon content of 2.75 percent, but difficult to get one of 3.75 percent, especially if a roof were used on the furnace. Richards[6] in the same discussion reports that the use of the roof was abandoned in order to obtain the high carbon content of 3 percent. Keller used a lime slag to effect desulphurization and to make possible easier electrical operation of the furnace. Since the work described in this paper was completed, Morrison[7] has reported that anthracite coal-slack containing 5 percent ash was a more effective carburizer than coke breeze containing 25 percent ash, and that crushed charcoal was superior to the anthracite coal, although charcoal in large pieces hindered carburization.

In addition to the direct effect of different kinds of carburizers the amount and the nature of the slag might be expected to have some bearing on the rate or degree of carburization. Intimate contact between the molten iron and the carburizer is of importance. Keller[8] found that ". . . . the introduction of a certain quantity of silica into the charge will increase the silicon in the product

[4] Turnbull, Robert, Electric pig iron in war-time. Trans. Am. Electrochem. Soc., 1917, **32**, 119.

[5] Turnbull, Robert, Electric pig iron after the war. Trans. Am. Electrochem. Soc., 1918, **34**, 143.

[6] Keller, Ch. A., Synthetic electric furnace cast iron. Trans. Am. Electrochem. Soc., 1920, **37**, 189.

[7] Morrison, W. L., Manufacture of synthetic cast iron in the electric furnace. Chem. and Met. Eng., 1922, **26**, 312.

[8] *Loc. cit.*

with a correspondent reduction of the amount of carbon therein." This reduction in the amount of carbon may have been due to the mechanical effect of the siliceous slag, and not to the introduction of silicon into the metal.

The available knowledge of the influence of some of the elements on the stability of cementite in the iron-carbon system naturally suggests the question of their effect on carburization during the production of synthetic cast iron. High silicon in blast furnace iron tends to produce graphite instead of cementite. The presence of silicon might, therefore, be expected to reduce the rate of carburization during the production of synthetic cast iron from steel. Manganese stabilizes cementite in cast iron but does not suppress the action of silicon to a marked extent.[9] Furthermore, alloys of iron and manganese, such as spiegeleisen and ferromanganese, contain more carbon than does pig iron, the carbon content usually increasing as the ratio of manganese to iron increases. Hence, it would be expected that the presence of manganese would assist in the carburization of iron, and increase the degree of saturation of carbon.

On the other hand, since sulphur is present in iron as manganese sulphide and also as iron sulphide if present in an excessive amount, it would therefore prevent the manganese and iron that it combined with from absorbing carbon. The percent of iron affected by the amounts of sulphur ordinarily met with in commercial practice would, of course, be so small that the actual decrease due to this cause in the amount of carbon absorbed would pass unnoticed. Phosphorus in solid solution in iron lowers the solubility of carbon, and it has been shown that, in the presence of silicon, phosphorus assists in the precipitation of graphite.[10] Heike[11] claims that small amounts of phosphorus favor the separation of graphite and that large amounts prevent it.

All of these factors have been considered in this study, although it has been realized that, due to the relatively small amounts of impurities usually met with, the effect upon the final total carbon would be small; also, that most of these effects have been determined from the cooling of cast irons, and in this study the

[9] Hoyt, S. L., Metallography, Part II, 1921.
[10] Hoyt, S. L., Metallography, Part II, 1921.
[11] Heike, Stahl u. Eisen, 1914, 34, 918.

reverse process has taken place. However, there was some likelihood that certain tendencies would be set up by the presence of the different impurities, and it was hoped that the foregoing information would be of assistance in determining the most desirable conditions for carburization.

The solubility of carbon in iron increases with the temperature. The results of the work of Ruff and Goeke[12] and of Ruer and Biren[13] show that the solubility of carbon in iron increases at the rate of 0.2 or 0.3 percent for each rise in temperature of 100 degrees, between 1200 and 1800 degrees Centigrade. Hence a difference in temperature of 100 degrees Centigrade would not be expected to have much effect upon the rate of carburization of iron. However, at the temperature of the arc in the electric furnace the solubility of carbon is relatively high, and, therefore, it is to be expected that carburization would be rapid in the metal directly beneath the arc. The direct arc by its stirring action should also aid carburization. High temperatures should be particularly desirable toward the end of the operation when complete saturation of the iron with carbon is being more nearly approached.

DESCRIPTION OF METHODS AND OPERATIONS

The following studies were conducted with the hope of determining some of the factors that influence the carburization of iron in making synthetic cast iron. They were first made in a small 2-electrode pit-type furnace, which held about 50 pounds of metal and took an input of about 50 kilowatts. The cross-section of the crucible was 9 by 15 inches. Three-inch square graphite electrodes were used. The furnace was first lined with magnesite brick and the bottom and sides then faced with magnesia-alumina spinel containing 2.5 parts dead-burned magnesia and 1 part alundum. The power input to this furnace corresponds to 2,000 kilowatts per ton of metal or 50 kilowatts per square foot of hearth area. Realizing that this furnace was overpowered, a larger furnace was constructed and used in repeating the experiments performed in the 50-pound furnace. The larger furnace was of the roofed, tilting type. It held 300 pounds of metal and

[12] Sauveur, Albert, The metallography and heat treatment of iron and steel: 1918, pp. 364-366. Sauveur and Boylston, Pub., Cambridge, Mass.

[13] Ruer, Rudolf, and Biren, Julius: Z. Anorg. Chem., 1920, **113**, 98.

took power at the rate of 75 to 100 kilowatts. The hearth was lined with magnesia brick and covered with magnesia-alumina spinel. The sides and roof were made of corundite brick, a highly aluminous fire clay, experience having shown that this brick gave more satisfactory results than silica brick. The cross-section of the hearth was 17 x 24 in. Two 3-inch round graphite electrodes were used. The power input corresponds to about 600 kilowatts per ton of metal, or 35 kilowatts per square foot of hearth area. When the furnace had been pre-heated to about 400 degrees centigrade, one thousand kilowatt-hours per ton was required for melting and carburizing to 3.5 percent carbon. Considering its small size, it would seem that the furnace was not overpowered to a large degree. The power factor was about 96 percent during all of the experiments.

The electrode consumption was at the rate of 11 pounds per ton of iron. Part of this consumption was due to oxidation of the electrode at the roof, since no cooling rings were used.

To determine the relative values of the various carburizers, most of the commercial forms of carbon were employed for comparison. The list includes graphite, resistor carbon, charcoal, coal-tar coke, low-ash coke, high-ash coke, silicon carbide, calcium carbide, and a lime-coke mixture to simulate calcium carbide. No anthracite coal was available.

The experiments cover many runs both in the small pit furnace and in the larger tilting furnace. For the work in the pit furnace mild steel turnings were used as the raw material. This material is similar to that used by Keller[14] in making synthetic cast iron. Fifty pounds of turnings per charge was used in all of the runs. In all tests the carburizer was crushed to pass a 10-mesh screen.

Before charging, the furnace was pre-heated to a red heat. The order of charging was as follows: About twenty pounds of the charge, consisting of alternate layers of steel turnings and carburizer, was put in the furnace. The current was then introduced, and the remainder of the charge added as rapidly as melting progressed. When the entire charge was melted, a sample for chemical analysis was ladled out and poured into a graphite mold one inch square and one and one-half inches long. Some of the metal was also poured on the concrete floor and covered with

[14] Keller, Ch. A. Synthetic electric furnace cast iron. Trans. Am. Electrochem. Soc., 1920, **37**, 189.

diatomaceous earth to prevent chilling. This latter piece was later broken and its fracture examined. Samples for analysis and fracture were taken every ten or fifteen minutes and when the fracture showed no further change, it was assumed that conditions had approached equilibrium and the charge was tapped.

In many of the runs in which the carburizer was added with the cold metal, the first sample taken after the charge was molten contained over 3 percent carbon. In order, therefore, to investigate the rate of carburization in the lower concentrations of carbon, it was necessary to melt the turnings in the absence of the carburizer, and then, after the first sample had been taken, to add the carburizer to the surface of the molten metal. It was more difficult to melt the steel turnings without the carburizer than with it, due to the relatively higher melting point of steel. The ferro-alloy and other additions were usually made with the first portion of the turnings, but at times they were made after the metal had been melted.

The carburizer was always added in excess of the amount theoretically necessary; usually it amounted to about 10 or 12 percent of the weight of steel turnings. In such a small furnace it was found to be a distinct disadvantage to have too thick a layer of carburizer on the surface of the melt, because the current would be carried through the carburizer without directly heating the metal. Hence, a layer of carburizer about one-half inch thick was kept on the surface, making sure, however, that there were no bare spots of metal exposed.

For experiments in the larger furnace, steel scrap in the form of boiler punchings and clippings was used, instead of the less pure steel turnings. The boiler punchings and clippings varied in size from one to ten inches, were uniform in composition, and contained 0.05 percent sulphur and phosphorus, 0.5 percent manganese, 0.5 percent carbon, and 0.2 percent silicon.

A charge in the large furnace consisted of 300 pounds of steel scrap and about 20 pounds of carburizing material. The furnace was pre-heated by placing a piece of electrode in the bottom and drawing an arc on it. Then about 200 pounds of the steel scrap and 10 pounds of the carburizer were charged, the carburizer being placed so that some of it rested between the pieces of steel and some lay on top acting as a cover. The furnace was operated

by direct arcing, and when most of the charge had melted an additional 100 pounds of steel scrap was added. The rest of the carburizer was added at intervals. The addition of ferrosilicon and other alloying material was made just before the metal was entirely melted.

The electrodes were controlled by means of a drum and worm-gear operated by hand. In order to insure arcs of equal intensity on both electrodes, two ordinary incandescent lamps were placed on a shelf near the meter board. These had a common connection to the metal bath and each a separate connection to one electrode. Thus, the brilliancy of the filament of each lamp was proportional to the voltage drop between the bath and the electrode to which that lamp was connected. This arrangement provided a sensitive and convenient means of regulation, assured smooth electrical operation, and thus made comparable the results obtained in the various runs.

The temperature of the bath of metal was taken at intervals throughout each run. A Leeds-Northrup optical pyrometer was used, two readings being taken by sighting first upon freshly-exposed metal and next upon the carburizer. These two readings checked very closely. The temperature was maintained fairly constant throughout all of the runs. It ranged between 1350 degrees and 1450 degrees Centigrade and was seldom higher or lower. Integrated temperatures for the various runs were not usually more than 50 degrees apart.

The experiments performed in the 50-pound furnace were repeated in the 300-pound furnace. In all, seventy-eight individual melts were made. Conclusions have been drawn from the results obtained in all of these tests. All the data cannot be reproduced here, and, therefore, only results of the typical runs will be shown.

The curves in Fig. 1 show the rates at which different forms of carbon are absorbed in molten iron and the relative values of these varieties of carbon as carburizers. The dotted portion of any curve is indefinite and covers the melting period. The carburization between 0.5 and 2.5 percent carbon has been largely ignored in this investigation for the reason that, throughout this range, absorption is so rapid that no appreciable difference in the various materials could be found. This is illustrated in Fig. 2. In these runs the metal was melted in the absence of carbon and

then graphite and charcoal, respectively, were introduced. In each case the carbon in the iron increased from 0.8 percent to 2.7 percent within 10 minutes. These were 50-pound charges, melted in the small pit furnace. Keller[15] states that the carburization of molten iron is very slow as compared with that of small solid particles of iron such as turnings. The tests just described and

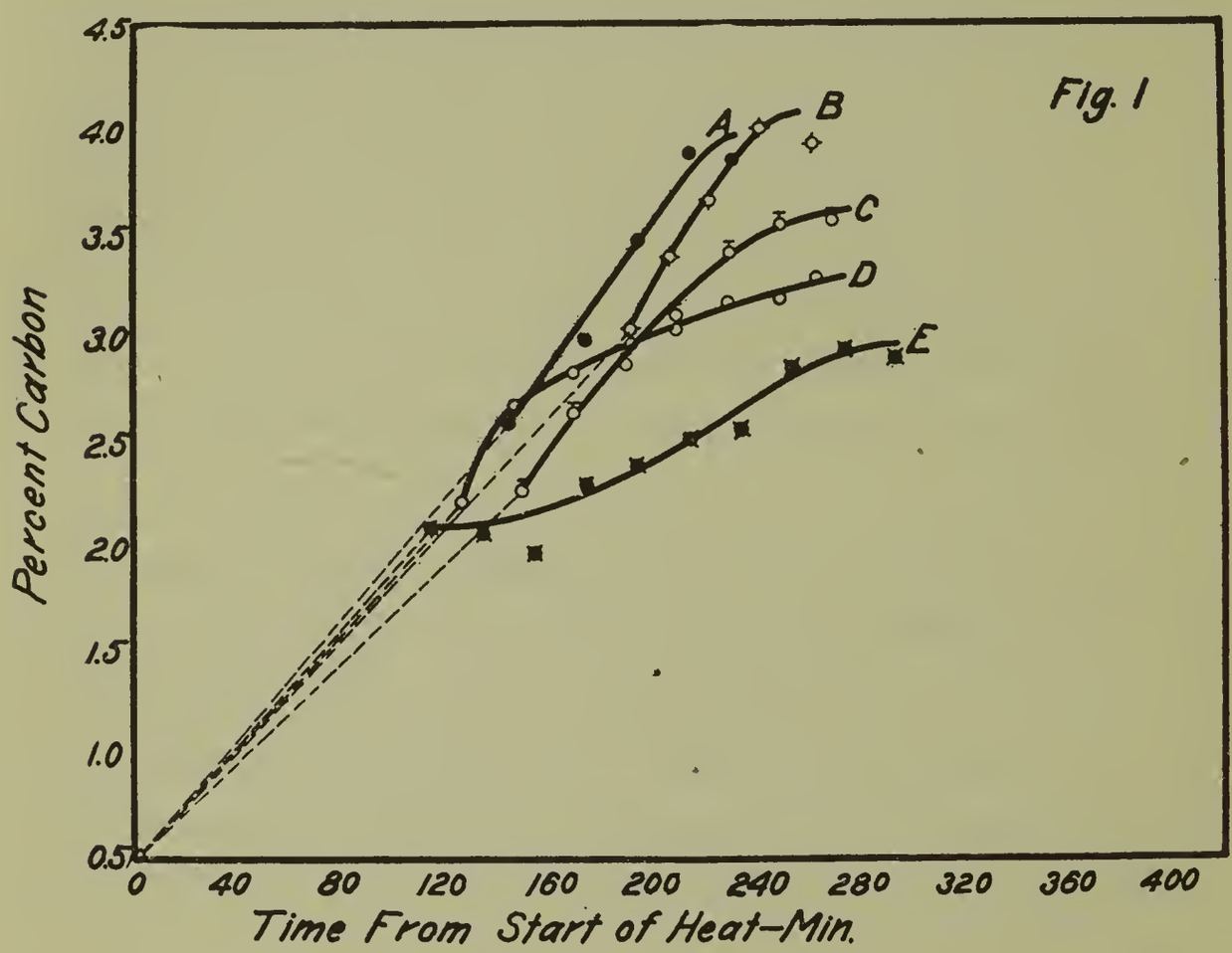


FIG. 1

Showing the rate of carbon absorption when using different forms of carbon. Silicon content about 2 percent in each case; other impurities low.

Key: A. Coal-tar coke.
B. Graphite.
C. Low-ash coke, containing 13 percent ash.
D. Charcoal.
E. High-ash coke, containing 25 percent ash.

other similar ones show that the rate of solution of carbon in molten iron is rapid, but naturally diminishes as the saturation point is approached. Furthermore, observations seem to indicate that carburization during the melting-down period is accomplished, not in the solid iron phase as intimated by Keller,[16] but in the liquid iron as it gradually forms and mixes with the carbon

[15] Keller, Ch. A. Synthetic electric furnace cast iron. Trans. Am. Electrochem. Soc. 1920, 37, 189.

[16] Ibid.

which at first is present in large excess. Results in the experiments here described have shown that there is little difference in the amount of carbon introduced whether melting small steel turnings or comparatively large boiler-plate clippings. The extreme slowness of the penetration of carbon in the cementation process is well known. It is, therefore, very probable that in making synthetic cast iron most of the carburization takes place after the steel has melted.

COMPARISON OF THE DIFFERENT VARIETIES OF CARBON

Graphite. Acheson granular resistor graphite was used in the tests. Graphite always gave a rapid rate and a high degree of carburization, in practically every case excelling all the other forms of carbon. The superiority of graphite over granular resistor carbon or coal-tar coke, which is similar to petroleum coke, was not very great. Curve B, Fig. 1, shows the carburization curve for graphite. The steep pitch of the curve and the high percentage of carbon obtained are particularly noticeable. The high apparent density of graphite undoubtedly assists it in obtaining good contact with the metal; its low ash content also unquestionably improves its carburizing power as will later be brought out more fully.

Charcoal. Curve D, Fig. 1, shows the rate of carburization using charcoal in the large furnace. Much lower absorption of carbon is shown here than in the charcoal curve in Fig. 2, which was obtained from a test in the small pit furnace. There was much better contact between the charcoal and the metal in the small furnace than in the large one. All the tests have shown that good carburization is possible only when good contact between the charcoal and the metal is obtained. Because of the light, porous nature of charcoal there is much difficulty in keeping it in good contact with the molten iron, especially near the arc or in the presence of a slag. The layer of charcoal on the bath should not be so thick as to prevent the arc from penetrating to the metal. In some types of furnaces, notably the pit-type furnace working continuously, charcoal should give satisfactory results.

Coal-tar coke and granular resistor carbon. The coal-tar coke, made by the distillation of coal tar, was obtained from a local

creosoting plant, and contains from 7 to 8 percent volatile matter and less than 4 percent ash. It is similar to petroleum coke and any reference made to it should apply with equal weight to petroleum coke. Curve A, Fig. 1, shows that coal-tar coke gives excellent carburization, more nearly approaching graphite than anything else that has been used. Fig. 3 shows a comparison of coal-tar coke with some other cokes. Granular resistor carbon

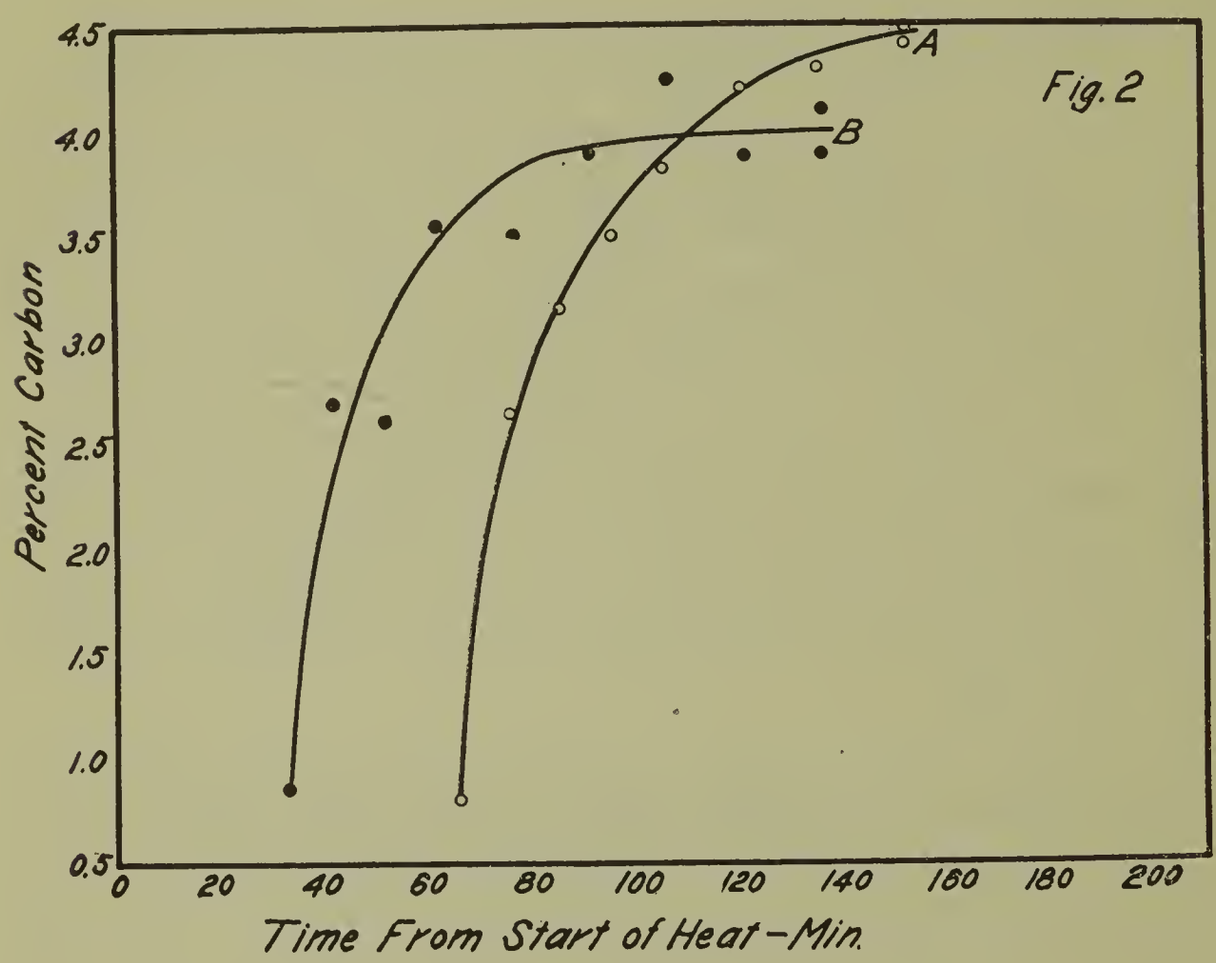


FIG. 2.

Showing the rate of carbon absorption at the lower concentrations of carbon. Tests made in small furnace on iron containing 2 percent Si.

Key: A. Using graphite as carburizer.
B. Using charcoal as carburizer.

containing 5 percent ash has given results similar to those obtained with the coal-tar coke.

High-ash coke. During the early experiments a high-ash coke was used for carburizing with consistently poor results, the maximum carbon content obtained in the iron being a little over 3 percent. This coke was so noticeably inferior that an investigation of the reason was undertaken. Analysis showed that the

coke contained 25 percent ash, and it was suspected that the trouble was due to this high ash content. Further experiments unquestionably proved that the high ash was the cause of the inferiority of the coke. A coke containing 13 percent ash gave much better carburization than did the 25 percent ash coke, but poorer carburization than did the lower ash coal-tar coke. Fig. 3 shows the relative rates and degrees of carburization obtained with

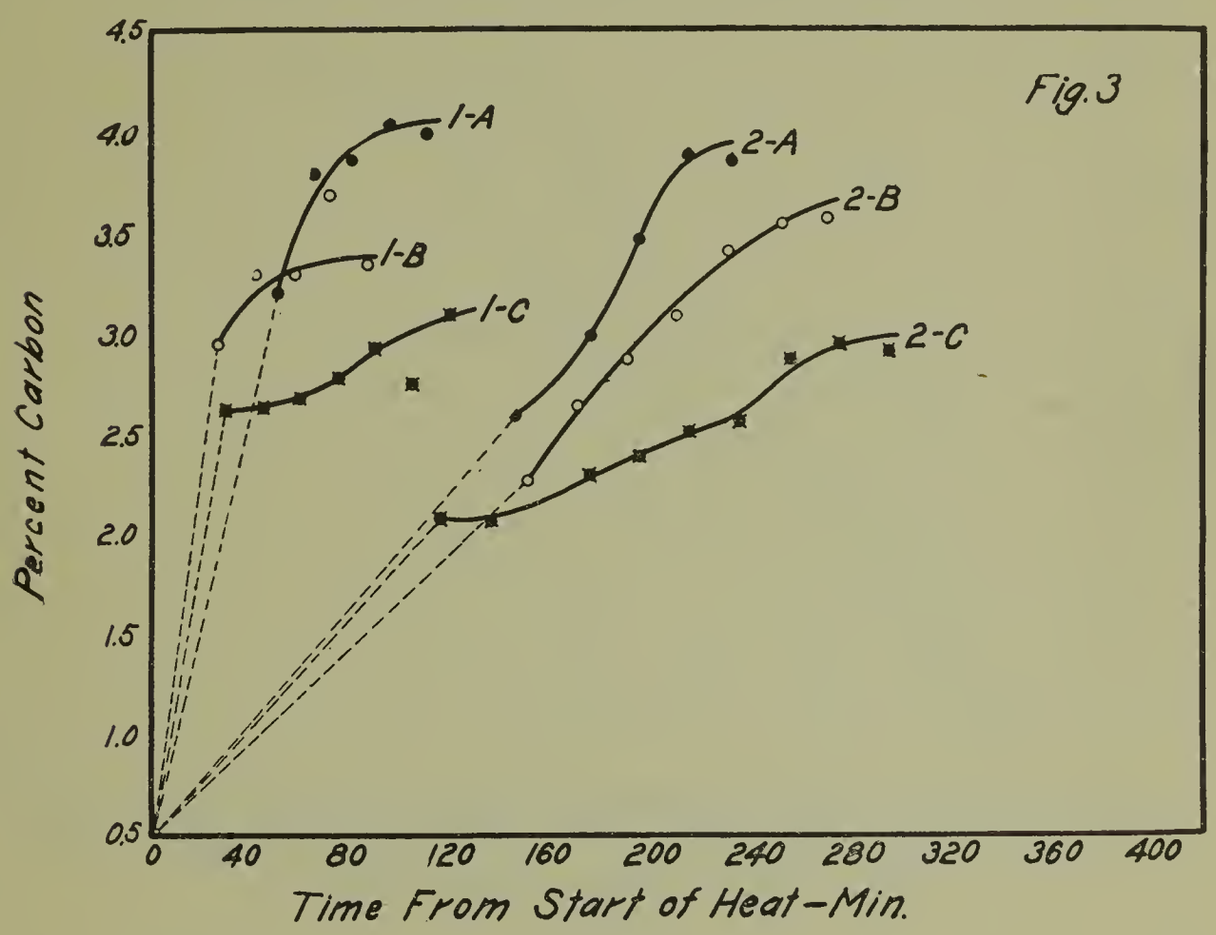


FIG. 3.

Showing the effect of ash content of carburizers on the rates of carbon absorption. Curves No. 1 from tests in 50-lb. pit furnace. Curves No. 2 from tests in 300-lb. roofed furnace.

Key: A. Coal-tar coke (Ash content under 4 percent).
B. Low-ash coke (Ash content, 12 percent)
C. High-ash coke (Ash content, 25 percent)

these cokes. Results obtained in the small and in the large furnace are shown. These curves illustrate the detrimental effect of ash, and show that the absorption of carbon decreases as the ash content of the carburizer increases. The ash being a component part of the structure of the coke probably acts as a protective coating on the carbon, serving to keep it from intimate contact with the metal, this effect being intensified as the carbon dissolves and the

relative amount of ash becomes larger. Graphite resistor carbon, coal-tar coke, petroleum coke, and charcoal should be desirable carburizers because of their low ash content. Of these, the denser varieties should be preferred.

Silicon carbide. Experiments with carborundum firesand (an impure silicon carbide) proved it to be an efficient means of intro-

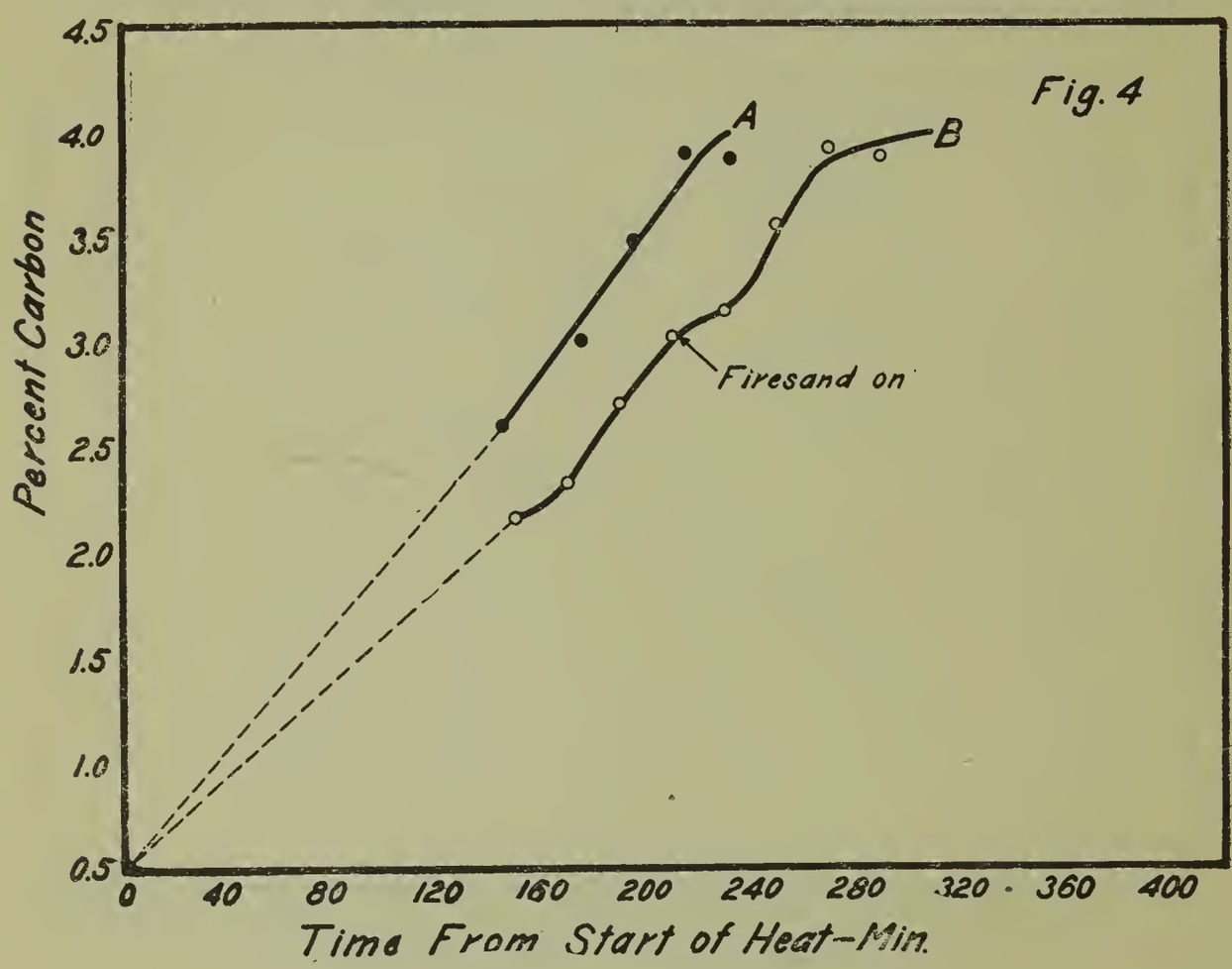


FIG. 4.

Showing the relative rates of carbon absorption when using coal-tar residue and carborundum firesand.

Key: A. Coal-tar as carburizer.
B. High-ash coke in first stage; firesand introduced as noted.

ducing both silicon and carbon into iron. Inasmuch as the proportion of silicon to carbon in silicon carbide is roughly 2 to 1, it cannot be used for introducing all of the required carbon because too much silicon would result. It would also be too expensive for this purpose. However, its cost for introducing silicon would almost equal that of ferro-silicon and it would have the added advantage of effecting some carburization. Fig. 4 shows the results of a test in which a high-ash coke and silicon carbide were

used in conjunction. The scrap-steel plate was melted with a cover of the coke and held molten for an hour. Previous experience had shown that after an hour there would be practically no further absorption of carbon from this coke. At this point, indicated by the arrow on the curve, carborundum firesand was thrown on the melt, with the result that the absorption of carbon continued rapidly until 3.9 percent carbon had been reached. Carbon and silicon were taken up by the iron in the ratio of 0.8 carbon to 1.55 silicon, which is very close to the proportion of carbon to silicon in silicon carbide. Assuming that the carborundum firesand contains 75 percent silicon carbide, the recovery in the iron of this silicon carbide as silicon and carbon was 75 percent.

In most cases it will be noticed that the last point in the curve is slightly lower than the preceding point. The last point is taken from the analysis of the pig sample, and the other points are taken from the analysis of the samples obtained in the graphite mold. Due to the slow rate of cooling of the pigs, those which contained large amounts of silicon or carbon ejected graphite as "kish" and hence contained less carbon than their equivalent samples which were cast in small molds, and therefore cooled too rapidly to permit the formation of so much graphite. The difference ordinarily amounts to about 0.1 percent carbon.

EFFECT OF SLAGS

In general all of the tests have shown that slags interfere with carburization. This interference is due to the physical effect of the slag in preventing contact between the carburizing material and the metal. Therefore, in the tests unless the effect of the slag was being particularly considered, the surface of the metal was kept as free from slag as possible. The effect of high ash coke has already been discussed (See Fig. 3). The ash from this coke consists essentially of alumina and silica. Curve F, Fig. 5, shows the effect of a high silica-alumina slag upon carburization with low-ash coke (coal-tar coke). This slag was accidentally introduced by the fusing of part of the furnace lining. Results of other tests have indicated the retarding effect of siliceous slags upon carburization.

High-lime slags have practically the same effect due to the physical action of tending to prevent contact. However, if conditions are right for the formation of calcium carbide, lime may aid carburization. Curve B, Fig. 5, shows the results of test with low-ash coke and a lime slag. Calcium carbide was formed by

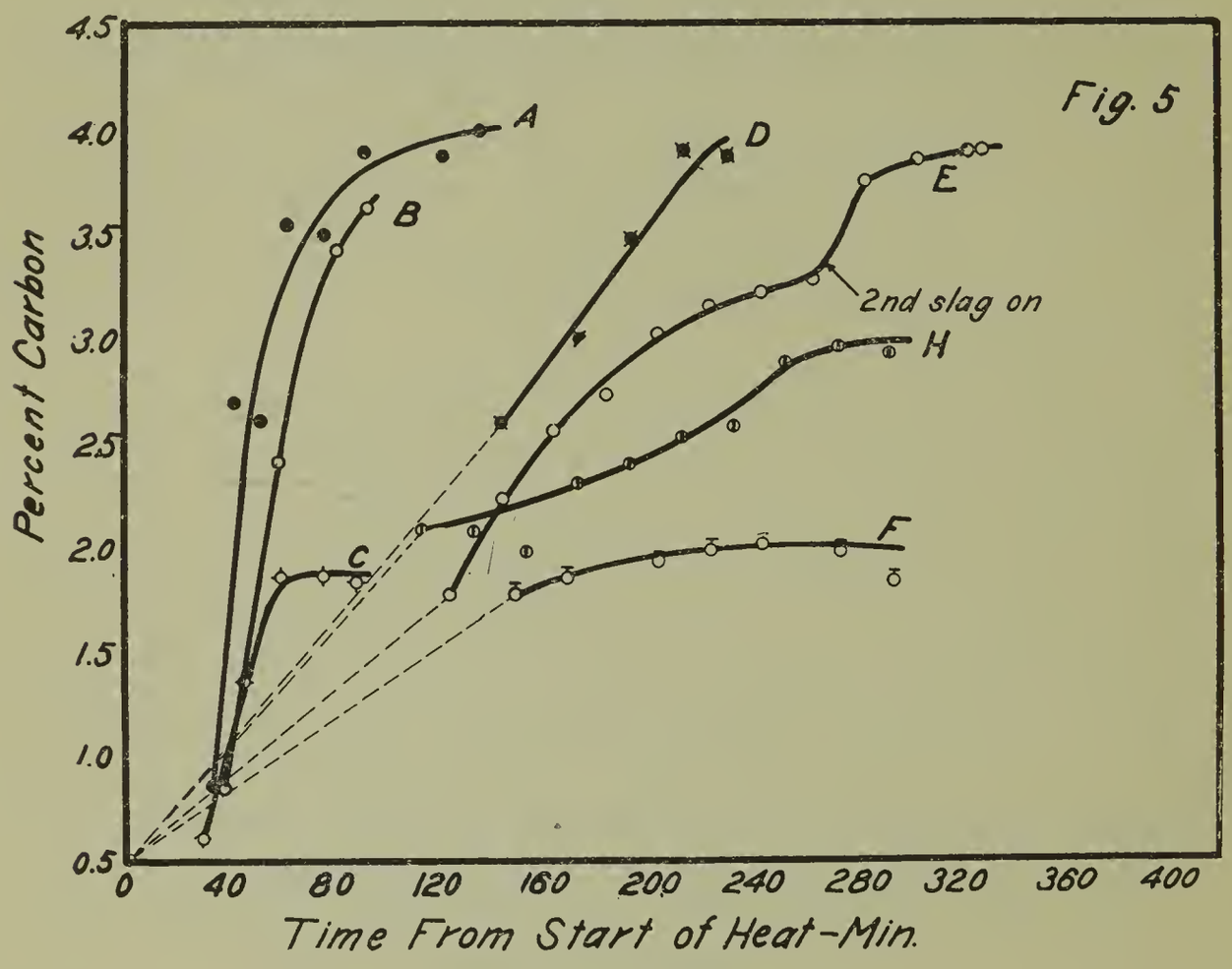


FIG. 5.

Showing the rates of carburization with and without slag.

Key: A. Run in small furnace using charcoal alone.
B. Run in small furnace using coke and a lime-fluorspar slag.
C. Run in small furnace using calcium carbide and a fluorspar slag.
D. Run in large furnace using coal-tar coke alone.
E. Run in large furnace using high-ash coke and a lime-fluorspar slag.
F. Run in large furnace using coke and silica-alumina slag.
H. Run in large furnace using high-ash coke alone.

the arc, thus causing rapid introduction of carbon into the iron. In another test using calcium carbide and carbon, carburization was still more rapid. Curve C is taken from an experiment in which calcium carbide alone was used as the carburizer. The carbon content of the iron increased rapidly and then stopped. Only 50 percent efficiency of the carbon in the carbide was

obtained, showing that either a large excess of carbide must be used, or that carbon must be charged along with the calcium carbide. Curves E and H, Fig. 5, show the effect of lime on a high-ash coke. Carburization proceeded fairly rapidly at first, but practically stopped until the first slag, which had by now largely increased in silica and alumina from the ash, was replaced by a fresh lime-slag.

EFFECT OF IMPURITIES

In studying the effects of the common impurities in cast iron, it has been found that innumerable combinations and concentrations from them are possible. In these experiments the effect of silicon in the absence of other added impurities was first studied. Then the effects of sulphur, phosphorus, and manganese in the presence of about 2.0 percent silicon, were investigated. Enough of the impurity was introduced to indicate its effect, but not enough to get too far away from concentrations that might be met in practice, although in a few instances an unusually large amount was used in order to intensify the effect.

Silicon. In these tests, the rates of carburization were about the same for irons containing 0.2, 2.0, and 7 percent silicon. Curves B and C in Fig. 6 show the rates of carburization of steel containing 2.0 and 0.2 percent silicon, respectively. The curve for 7 percent silicon is not shown here, but its slope is very much the same as the slopes of curves B and C. Thus it is seen that the content of silicon had no effect upon the rate of absorption of carbon by molten iron.

Silicon does, however, affect the maximum possible absorption of carbon. Fig. 7 shows the relation between silicon and carbon, the points on the curve representing the maximum carbon content of samples of iron containing various amounts of silicon, at 1450° C. These values were obtained from samples taken from a bath of metal held at this temperature, in contact with carbon, until its carbon content remained unchanged for one hour. The samples were chilled to prevent any reduction of the carbon content by the ejection of "kish" during cooling. There was practically no difference between the carbon content of the chilled samples and that of the slowly cooled pig samples in 0.2

and 2.0 percent silicon runs, but there was a difference of 0.46 percent in the case of the 7.0 percent silicon run. It will be seen from Fig. 7 that an increasing content of silicon decreases the maximum absorption of carbon obtainable, but that even with 5 percent silicon it is still possible to have 4 percent of carbon, and, therefore, the practical effect in ordinary cases should not be very marked.

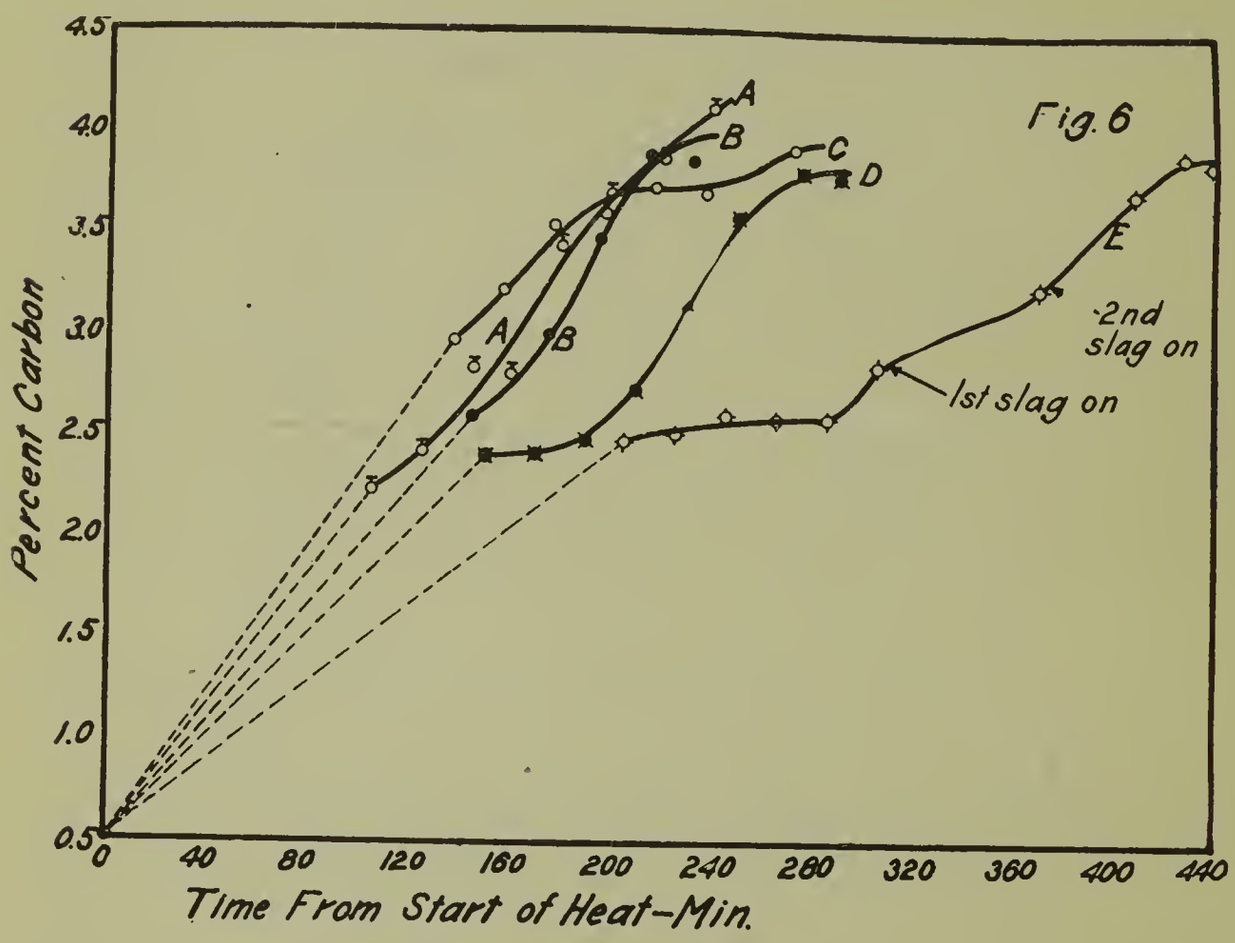


FIG. 6.

Showing effects of impurities on the rate of carbon absorption. Two percent silicon in all except C. Manganese, phosphorus, and sulphur are low except as indicated below.

		Percent
Key:	A. Manganese	1.75
	B. Silicon	2.0
	(other impurities low)	
	C. Nearly pure iron.	
	Si	0.2
	Mn	0.4
	S and P	0.5
	D. Phosphorus	0.70
	E. Sulphur	0.75

Manganese. Curves A and C in Fig. 6 show the rates of carburization for high manganese and low manganese irons, respectively. By low manganese is meant 0.40 percent and by high manganese, 1.75 percent. Curve A has a steeper slope than

Curve B, indicating that manganese is beneficial. These curves are plotted from results obtained in the large furnace and are substantiated by data gathered from tests in the small furnace, not described here. Although the results show a distinct effect, it may not be large enough to warrant the statement that manganese is beneficial. However, it is to be expected that man-

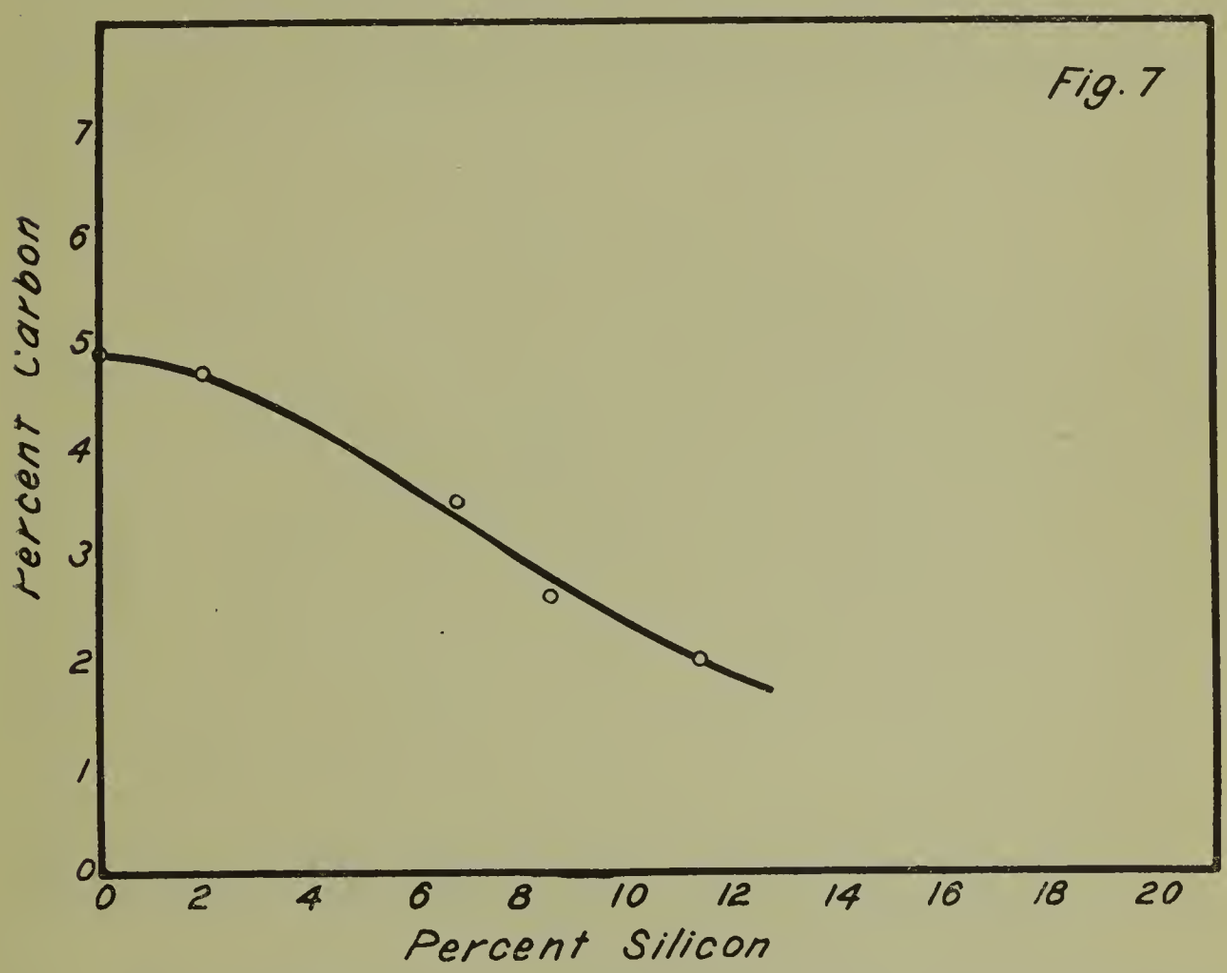


Fig. 7. Solubility curve of carbon in iron containing varying percentages of silicon at 1450° C.

The point corresponding to zero percent silicon was taken from Ruer and Biren[17] and Ruff and Goeke.[18]

ganese aids the carburization of iron. Experiments are now being conducted to bring out further data upon this point.

Sulphur. It is not to be expected that sulphur would materially affect the absorption of carbon by iron. However, during this investigation, the effect of sulphur has been strikingly noticeable. Sulphur has always appeared to retard the rate of carburization and decrease the total absorption of carbon. Curve E in Fig. 6

[17] Ruer, Rudolf, and Biren, Julius: Z. Anorg. Chem., 1920, **113**, 98.

[18] Sauveur, Albert, The metallography and heat treatment of iron and steel: 1918, pp. 364-366, Sauveur and Boylston, Pub., Cambridge, Mass.

and the curves in Fig. 8 are plotted from results obtained in a test in the large furnace, in which 0.8 percent sulphur was introduced during the melting period. Fig. 8 shows that the absorption of carbon had practically ceased when the first desulphurizing slag was added, after which it increased regularly as desulphurization continued. The effect of sulphur on the rate of carburization is shown in Fig. 6. From an examination of the results obtained

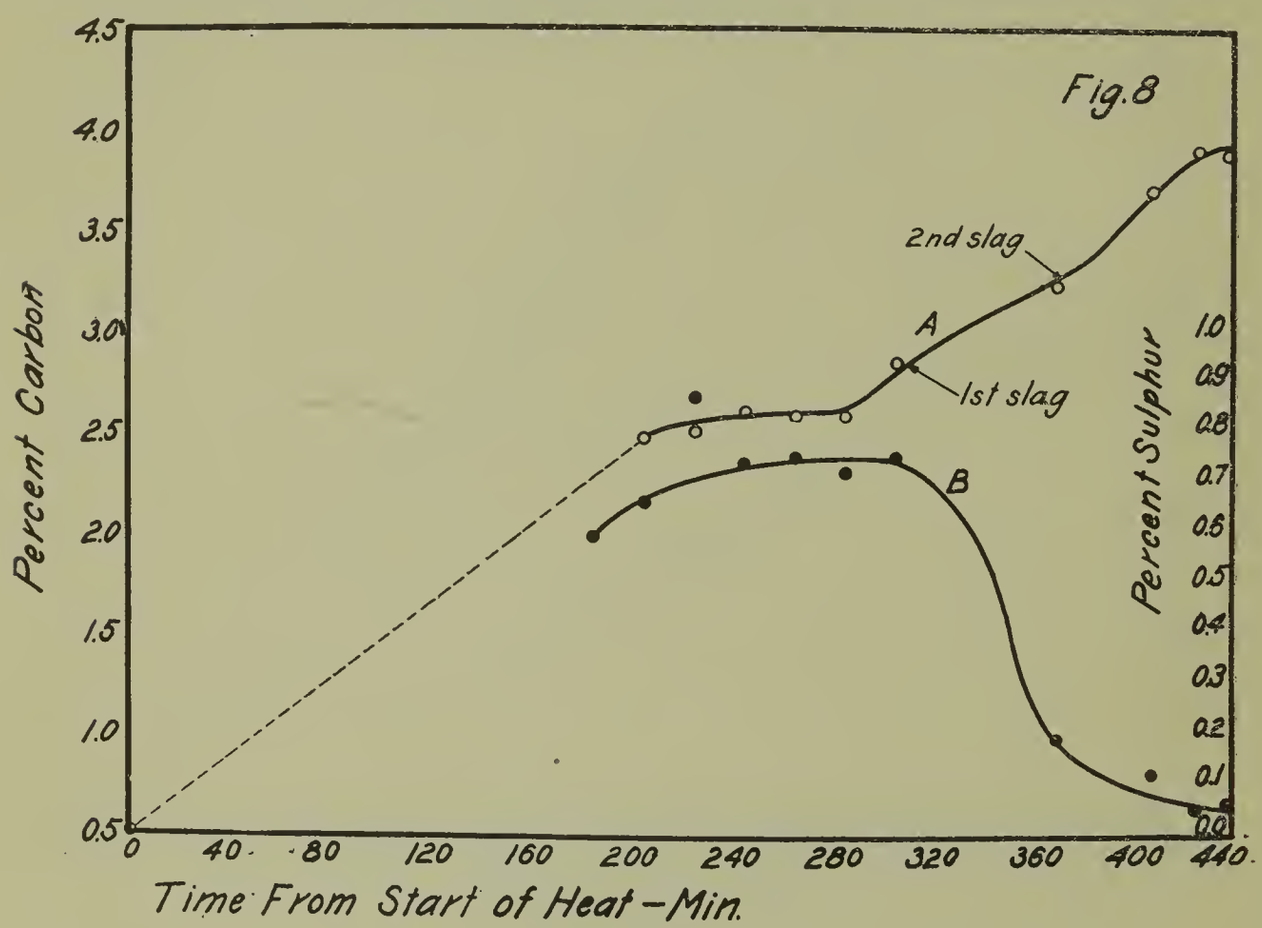


FIG. 8.

Showing the relation between carbon absorption and sulphur content. Sulphur was eliminated and carbon introduced toward the end of the heat by two successive carbon-lime-fluorspar slags.

Key: A. Carbon curve.
B. Sulphur curve.

in several other tests, not described here, the deleterious effect of sulphur is evidenced when the sulphur content is as low as 0.1 to 0.2 percent, although the effect is not so marked as in the example discussed above.

It is surprising that sulphur should have such a marked effect, and it is not improbable that further work may show that something other than sulphur is responsible. However, the results of the present study show very plainly that in the tests here described sulphur retards the carburization of molten iron.

Phosphorus. The study of the effect of phosphorus shows that it probably does not influence carburization. Curve D, Fig. 6, showing the results of the high phosphorus (0.75 percent P) run, has an average slope of approximately the same degree as have the curves for the phosphorus-free runs. The slow rate of carburization at the beginning of this test was undoubtedly due to the presence of some slag, because when this slag was removed absorption of carbon took place rapidly. In other tests performed in the small furnace, phosphorus showed practically no effect upon the rate of carburization.

CONCLUSIONS

1. The results indicate that the carburizing ability of different forms of carbon decreases as the ash content increases and that the denser varieties of carbon are more effective than the more porous ones. Artificial graphite, resistor carbon, petroleum coke, and coal-tar coke give better results than the higher ash cokes or charcoal. Although the low ash content of charcoal would put it in the class with graphite, its porous nature prevents good contact with the metal. Graphite, because of its lower ash and higher density, has given slightly better results than any of the other forms of carbon used.

2. The presence of slag decreases the rate of carburization by tending to prevent contact between the metal and the carburizer. This action is more pronounced as the acidity of the slag increases. Lime slags counteract the deleterious effect of the high ash in coke, and, if conditions are right for the formation of calcium carbide, aid carburization.

3. Silicon carbide is an excellent medium for adding both silicon and carbon to iron. It cannot be used for introducing all the carbon because too much silicon would be carried into the metal and also the cost would be too high. Silicon carbide should be used in the comparatively inexpensive form of firesand and in conjunction with one of the low-priced carburizers, such as coke.

4. Silicon has no effect upon the rate of carburization, although it does decrease the maximum possible absorption of carbon.

5. Manganese seems to increase both the rate and the degree of carburization, although this increase is so small as to be

negligible for the amounts of manganese ordinarily met with in commercial iron.

6. Phosphorus has no effect upon the rate or the degree of carburization, although, like silicon, if present in large quantities, it may decrease the content of the total carbon in the pig.

7. Sulphur probably decreases the rate and the degree of carburization.

8. An increase in temperature from 1350 to 1450 degrees Centigrade has no noticeable effect upon the carburization.

9. Carburization takes place practically entirely after the metal has been melted.

ACKNOWLEDGMENTS

Much credit is due Mr. B. M. Larsen, "fellow" in electrometallurgy, University of Washington, and Mr. A. E. Anderson, junior metallurgical chemist, U. S. Bureau of Mines, for assistance with the experimental and analytical work. Grateful acknowledgment is made to the College of Mines of the University of Washington for the use of its laboratory facilities, and to members of its faculty for helpful cooperation. The authors also wish to express their appreciation for the helpful encouragement and criticism received from Messrs. D. A. Lyon and O. C. Ralston of the U. S. Bureau of Mines.

DISCUSSION.

Clyde E. Williams: We also showed in recent experiments that carburization proceeded much more rapidly when the carburizing material was put on the bottom of the furnace under the scrap steel. The steel would melt down onto the carbon and carburization would take place rapidly. This was the case only when the carburizing material used contained no volatile matter.

Bradley Stoughton[1]: I do not suppose there is any subject more important than this carburization in the manufacture of synthetic cast iron. Probably everyone of you knows that attempts made on the Pacific coast to manufacture a synthetic cast iron

[1] Consulting Engineer, New York City.

in the open hearth furnace failed because they could not make enough carbon dissolve in the iron. We had to get temperatures available in the electric furnace before the process could be a success on an industrial scale. I notice one thing in this paper which surprises me a good deal, and I think perhaps the authors would like to explain it. On page 65 they say "sulphur is present in iron as FeS." Well, it is in bad iron, but good cast iron never has sulphur present as FeS. A foundryman puts twice as much manganese in iron as sulphur, with the very object of having MnS instead of FeS. If the authors overlooked that point and had FeS in their iron, it may explain this unexpected behavior of sulphur. Perhaps Mr. Williams can say something about that before we go on.

Clyde E. Williams: In connection with that, we were referring to the very high quantities of sulphur that would be present. As I said, we conducted these experiments with larger proportions of impurities present than would ordinarily be met with. In the work on sulphur we had up to 0.8 percent sulphur in an extremely low manganese product, so that we would obtain the effect of the sulphur alone. Hence, I should say that in this case the bulk of the sulphur was present as iron sulphide.

Frank Hodson[2]: I would like to ask the authors if they considered putting this sponge iron directly into an electric furnace, probably mixed with scrap, with the idea of making an iron lower in carbon than the average gray iron? I think the results of these experiments would be of very great interest to everybody.

Clyde E. Williams: We have not gone into the melting of sponge iron sufficiently to say much about that. We took up this investigation just as a preliminary study of the carburization of iron with the hope that the results would be of assistance in the major problem—the melting of sponge iron. However, we have been able to melt a sponge iron product that contained about 80 percent metallic iron very successfully, introducing about 3 percent carbon.

Robert Turnbull[3]: I would like to compliment the authors on this paper, which is a wonderful follow-up of the work done

[2] President, Electric Furnace Const. Co., Philadelphia, Pa.
[3] Managing Director, U. S. Ferro Alloys Corp., Niagara Falls, N. Y.

during the war. Their recent work, by further experiment, bears out what was accomplished during the war. The authors were perfectly right in saying that we used silicon carbide as our final carburizing agent, in the form of "firesand." We arrived at this by reason of the fact that we used, first of all, charcoal in the lump state, and owing to its being in this form, it did not get into close enough contact with the metal, and it was rare that we got our carbon over 2.5 percent. We then began to crush our charcoal, thereby insuring a closer contact with the metal, and immediately reached 3 percent and over. The idea then came to us, that by the use of silicon carbide as the carburizing agent, in the form of "firesand," we would not only get better carburization, but the required silicon would also be furnished by this material. This was the case, and we cut out entirely the use of ferro-silicon. I do not agree with Mr. Williams in regard to the cost of adding the silicon, unless the Carborundum Co. have increased their price of "firesand." The final cost to us of the silicon addition to the metal was exactly half when using "firesand," as when using ferro-silicon.

Colin G. Fink[4]: I merely want to refer to figure 4 on page 74. The authors state that the moment the "firesand" was added the carbon content went up. If we omit the next two points and the point marked "firesand," we obtain a straight line. Perhaps the kink in the curve was due to a cooling effect. In your ordinate you are dealing with very short time intervals.

G. K. Elliott[5]: I have had some experience in carburizing low-carbon iron in the electric furnace which verifies many of the points brought out in this valuable contribution. I only wish it had been written several years earlier when it would have saved me much troublesome investigation. Especially is the point about sulphur reducing the rate and degree of carburization parallel to my experiences. I have seen iron with 0.03 percent sulphur carburized to 3.90 percent by a combination of high temperature, low-ash coke and a long hickory pole for stirring, which last expedient Mr. Cawthon has mentioned in his very instructive paper. The retarding effect of sulphur is puzzling, but possibly

[4] Consulting Electrometallurgist, New York City.

[5] Chief Chemist and Met., The Lunkenheimer Co., Cincinnati, Ohio.

can be explained in part by considering the following facts: That sulphur exists as manganese sulphide, that the rest of the manganese is united with carbon forming carbide, that a reduction of sulphur is substantially equivalent to an increase of manganese, and finally that an increase of manganese is known to assist the dissolving of carbon in iron. In other words, it is probable that low sulphur influences carbon indirectly through their mutual relation to manganese.

As a matter of explanation and in reply to Mr. Hodson, I wish to say that my deductions regarding the use of the electric furnace for cast iron in England were based upon the discussion of the exchange paper written by me for the Institution of British Foundrymen last year, in which discussion, although evidently very representative and exceedingly extended, there was only one vague and rather discouraging reference to this use of the electric furnace in England.

Bradley Stoughton: Of course the cupola iron will take up 1.5 to 2 percent of carbon. What has been your experience, Dr. Moldenke, as to the highest you can get in the cupola?

Richard Moldenke[6]: My experience in running straight steel heats, under regular melting conditions, is a maximum of 2.50 total carbon in the resulting castings. It is quite possible, however, to compel the absorption of more carbon by using an excess of fuel with the steel very thin, as in the case of making sash weights from tin cans. Here the cans are dumped directly into the cupola, and it requires about a pound of coke to every two and a half pounds of tin cans to do the work properly. Ordinary melting uses one of coke to eight of metal. In a recent test run, however, in which I used half the fuel of petroleum coke, I managed to get 3.10 total carbon in the metal made from all steel charges. Any information giving methods of getting high carbon percentages into molten steel easily will be of great interest to the foundry.

The subject of synthetic pig iron is attracting special attention. In Germany a large tonnage of this metal is now made, by melting briquettes of cast borings and steel turnings with ferro-silicon encased in cement. These briquettes are made with the borings

[6] Consulting Metallurgist, Watchung, N. J.

heated red hot under reducing atmosphere conditions, and consolidated under the steam hammer. The resulting pig iron does not run over 2.5 in total carbon, and is used in the production of malleable castings and "high test" cast iron.

Robert Turnbull: I can give you an illustration of cupola practice from New Zealand. A firm of steel manufacturers there, was unable to procure any low phosphorus pig iron for use in their Bessemer converter. To overcome this, they used a charge in their cupola composed of miscellaneous steel scrap, a small quantity of pig iron and in order to create the reducing atmosphere, which Mr. Moldenke referred to as being necessary in the making of the briquettes, they added a certain amount of 50 percent ferro-silicon. With this mixture they produced a good grade of pig iron, which they eventually used in their Bessemer converter.

Clyde E. Williams: In explanation of Dr. Fink's question, although it is true that there is practically no change in the slope of Curve B, Fig. 4, after carborundum "firesand" was added, there would have been a marked change had the "firesand" not been added. Many previous experiments using high-ash coke gave curves that rose rapidly until 2.0 percent to 3.0 percent carbon was reached and then flattened out. See, for example, curve E, p. 70. In the case under discussion, the "firesand" was added at the point where it was expected that this flattening out would begin. The continued abrupt rising of the curve was, therefore, caused by the silicon carbide and would not have taken place without it.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, Mr. Bradley Stoughton in the Chair.

THE MELTING OF CAST IRON IN THE BOOTH ROTATING ELECTRIC FURNACE.[1]

By H. M. Williams and T. B. Terry[2]

Abstract.

The subjects discussed in this paper are refractories, electrodes, power, rotation, charging, slagging, temperature control, pouring and metal losses.

A number of analyses are given which show the effect of melting on the chemical composition. Comparative physical tests are given of heats of cast iron made from borings, pig and back scrap, and all back scrap. The effect of steel and alloy additions on the physical properties are shown in tests of several typical heats.

A Booth rotating electric furnace was installed in the experimental foundry of the General Motors Research Corporation in September, 1920. The furnace is of the regular standard type, and has a capacity of from 114 to 125 kg. (250 to 280 pounds) of metal. This furnace has been used exclusively for the melting of cast iron. To date 750 heats have been melted.

The original purpose of this installation was to have available a small unit which could be used for the melting of either ferrous or non-ferrous metals. The installation consists of a base and two shells; one for the melting of ferrous, the other for non-ferrous metals. In actual service both shells have been used for the melting of cast iron, one shell always being lined and available in case of emergency, such as the failure of the lining in the shell in use. The shells can be changed in about one hour.

In the study of the various analyses of cast iron, it was found

[1] Manuscript received April 5, 1922.

[2] Research Department, General Motors Research Corp., Dayton, O.

desirable to have some way to utilize the iron which was melted, and a molder was put on for this purpose. As we have our own pattern shop at this plant, and a large number of grey iron castings are required from day to day, it was soon found that it would be convenient to produce a larger quantity of these castings in the experimental foundry. As a consequence we now have four molders and two core makers, who are engaged in the production of molds for castings. The iron is all melted in the

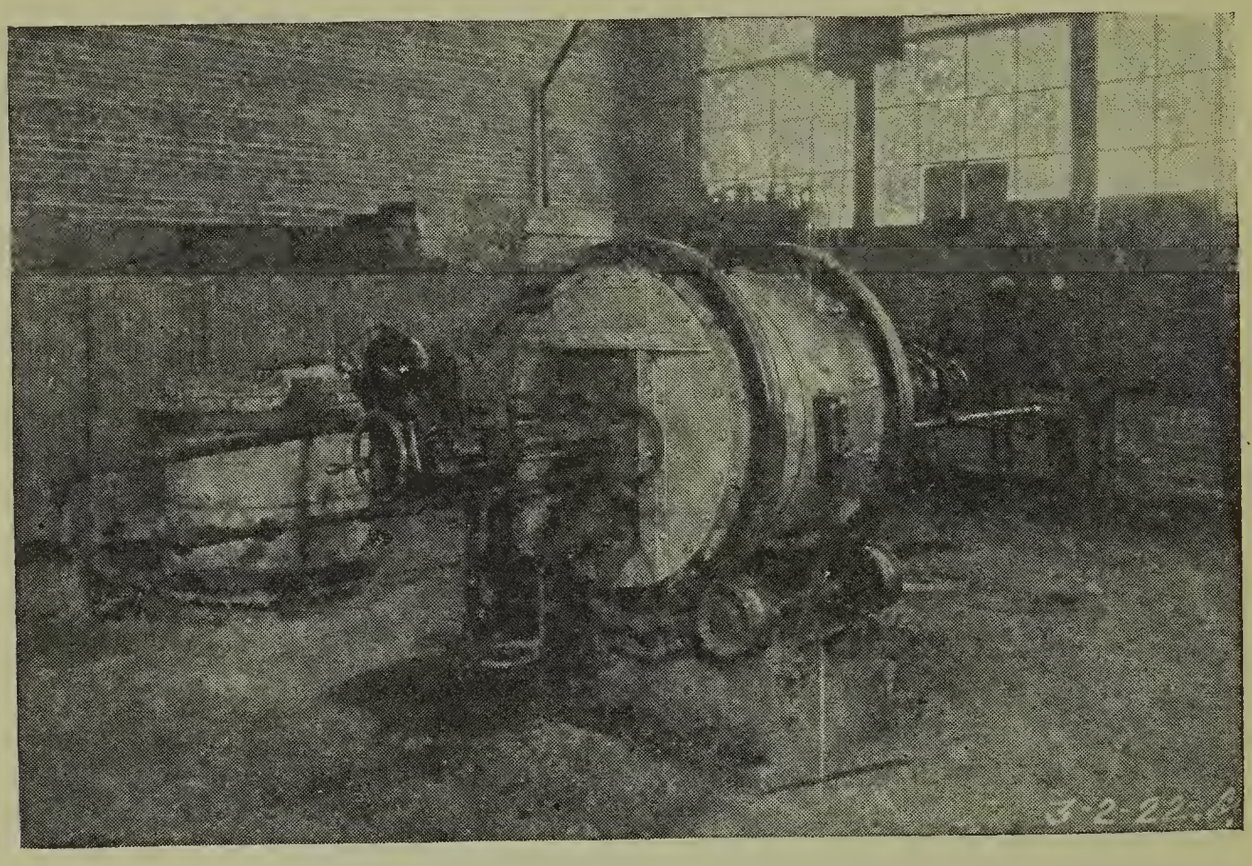


Fig. 1. The Booth Rotating Furnace

Booth furnace, which has averaged 15 heats per week, and as many as five heats per day have been made in rush periods.

TRANSFORMER AND CONTROL.

The furnace is equipped with a Pittsburgh transformer of 75 KVA capacity. It operates at 6600 volts on the high tension side, and is provided with taps for 115, 100, 90 and 80 volts on the low tension side. The automatic electrode control is made by the General Electric Company. Its operation has been entirely satisfactory.

REFRACTORIES

The tiles used for linings in this furnace are made by the Laclede-Christy Clay Products Company. We are using tiles made from Suprafrax, which is a high alumina clay, supposed to be neutral in its reaction.

In the early operation of this furnace, and on account of the shape of the tiles and our lack of proper equipment for charging, we obtained approximately 80 heats per lining. The lining cost at this rate is high. We have been able by a change in the shape of the tile, namely, recessing the cylindrical tile into the end tiles, and with suitable charging equipment and furnace attention, to obtain as high as 225 heats before it was necessary to replace the lining. These furnace linings are operating exclusively on cast iron, and in temperature measurements taken with an optical pyrometer, we find that the lining is heated as high as 1760°C. (3200°F.).

In the operation of the furnace, it is necessary to watch the linings carefully and patch any holes as quickly as possible. A number of materials have been used for this purpose:

Suprafrax cement

Suprafrax cement and carbo sand in equal parts

Carbo sand and fire clay, proportion two to one and three to one respectively. We have found that the latter mixture is superior for hot patching.

We had difficulty at first with the iron penetrating through the joint between the cylindrical tile and the end tile, but by recessing the cylindrical tile into the end tiles, this difficulty has been entirely overcome. As an additional precaution, in building up the lining, we put in a fillet of Suprafrax cement in each end. This strengthens the corner and also prevents the iron from penetrating the joint.

ELECTRODES

The electrodes used are standard Acheson 63 mm. (2.5 inches) diameter graphite electrodes joined with nipples. The electrode consumption of the first heat averages about 0.6 kg. (1.25 pounds) and of subsequent heats about 0.3 kg. (0.62 pound) per 114 kg. (250 pounds) charge.

In the early operation of this furnace, the electrode breakage

was excessive on account of the operator not being sufficiently skilled in knowing just when to start rotation. If rotation is started too soon, the unmelted chunks of metal will be carried up on the sides and fall back, breaking the electrodes.

POWER.

The furnace is operating on the 90-volt tap, and the regulator is set for 1000 amperes. We are able to get 60 kilowatts per hour input into the furnace at this setting. On Monday mornings 100 Kw. H. are used to preheat the furnace before charging. After this

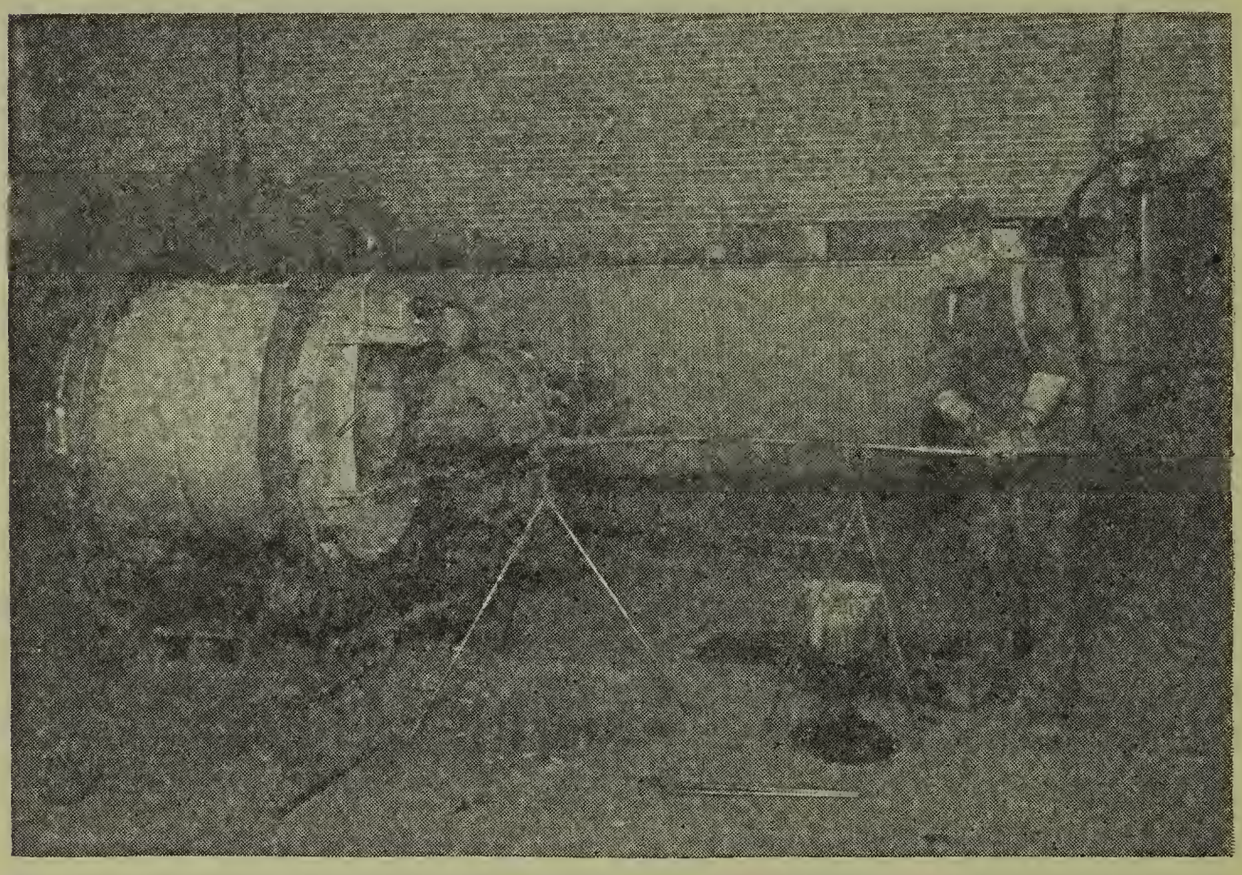


Fig. 2. Special Device for Charging Pig.

preheat, the first heat is taken off with an expenditure of from 145 to 165 Kw. H. On other week days the furnace is charged after the last heat of the day and let set overnight with no current on. The first heat is taken off the following morning with an expenditure of 165 to 175 Kw. H. In melting borings, the first heat is taken off in about 2 3/4 hours using 170 Kw. H.; the second heat in 1 1/4 hours using 80 Kw. H.; the third heat in 1 hour 10 minutes using 70 Kw. H. These figures will be influenced by time lost in delays, such as waiting for molds, etc.

ROTATION.

After having determined the amount of energy input necessary to melt the charge, it is a simple matter to avoid electrode breakage due to rotation. After sufficient energy input, the operator gives the furnace three or four half turns and watches the ammeter for any surge. If none, the charge is sufficiently melted to proceed with rotation.

A great deal has been said with regard to the fact that rotation does not mix the melt. If the melt were in a true cylindrical container, this would no doubt be true but on account of the irregularities on the inside surface of the cylindrical lining, we have found that the charge is very thoroughly mixed. We have not been troubled with segregation in any of our castings.

MELTING DATA.

Charging—In Figure 2 is a view showing the special device which has been found very satisfactory for charging pig and large pieces into the furnace. Such materials as borings, steel punchings and small castings are thrown into the furnace with a shovel. In making up special analyses where an addition of a ferro alloy is required, we have made up a device which will allow us to add this material through the electrode hole.

It is found that in charging overnight, the charge should be made up of pig and heavy castings, rather than material like borings, which oxidize badly and cause a loss of carbon and silicon.

Slagging—On account of the construction of this furnace, it is practically impossible to handle a slag. For this reason, no fluxing material is added with the charge. Any slag which is obtained is probably a combination of iron oxide and the lining. It is necessary from time to time to pull out a small quantity of this material after a heat is poured.

Additions—The construction of this furnace makes it difficult to make additions to the charge after melting has started, and it is impossible to look in and see the condition of the bath at any time unless the door is opened, which causes the interior to cool down rapidly. For this reason we have generally made up our

mixtures as complete as possible, and charged them at once into the furnace. Deoxidizers or small additions are made through the electrode hole as noted above.

Pouring—The pouring is done by catching the metal in heated hand ladles supported on special fixture shown in Figure 1, and pouring in regular manner. It is important to have the ladles well heated before receiving the iron. The first ladle of iron is not as hot as the second and subsequent ladles on account of the iron having to run out over the cold spout.

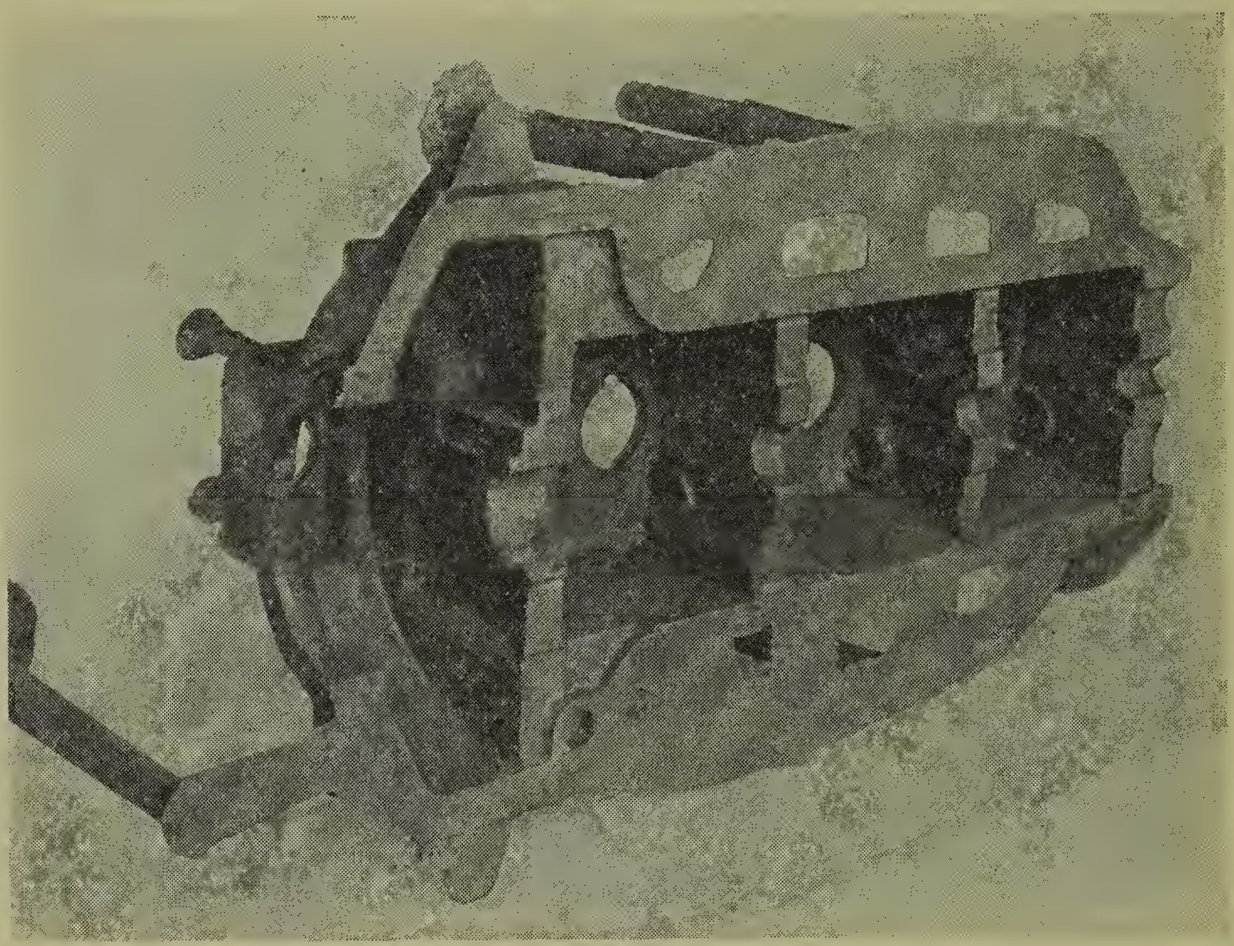


Fig. 3. Crank Case Casting.

Temperature Control—The temperature control of the metal is accomplished by paying strict attention to the power, that is, the higher the power the higher the temperature. By experience with the types of castings to be made, the sections, composition, etc., and with proper preheating of ladles, we have been able to obtain satisfactory casting conditions.

Specifications for grey iron used in automobile practice call for very low phosphorus content, which means less fluidity, and consequently a higher pouring temperature. Figure 3 is a view of a

crank case made from iron with 0.04 percent phosphorus, carbon 3.00 percent and silicon 2.50 percent. This view is shown to call attention to the high heat which must be necessary for the casting of thin sections with long runs from metal of this analysis. The metal thickness in this case is 4 mm. (0.16 inch).

Losses—The metal losses were determined by weighing the charge into the furnace against the weight of castings, gates, sprues, etc., recovered. It is necessary to take an average figure for this value, as it often happens that it is impossible to drain the furnace completely after each heat. This difficulty is due to wear of lining, slag running down into pouring hole, etc. With pig iron and back scrap charges, the recovery has averaged 96 percent. When operating on clean borings, free from rust, the recovery has run from 92 to 94 percent.

As far as we are able to find by careful analysis, the loss in chemical elements of the materials used in the charge and of the heats poured is negligible. The tests recorded in Table I are cited on this point.

It should be noted that in the case of the heat of all borings, where it is possible to obtain a representative sample that the differences in analysis of the material charged and the heat poured are within the limits of error of chemical analysis. In the case of all-pig heats, it will be noted that there is a marked difference in the analysis of pigs from the same shipment. For instance in Lot No. 13, the carbon ranges from 3.35 to 3.81 percent while the silicon varies from 2.97 to 3.57 percent. Manganese, phosphorus and sulphur are quite constant, at least within the limits of error of sampling and chemical analysis. In spite of these variations, the actual analysis differs from the estimated analysis at most, only 0.14 percent of carbon and 0.15 percent of silicon.

PROPERTIES OF THE IRON.

This type of furnace is ideal for the handling of borings, turnings, etc. As soon as the material is charged, rotation can be started which constantly turns over the material preventing melting of a pool in the top of the charge.

The quality of the borings must be good; the borings should be stored inside to prevent rusting. Rusty borings will cause

TABLE I. *Loss of Chemical Elements in Electric Furnace.*

	T. C.	Mn.	Si	P	S
Heat No. 748—Borings Charged					
Charge analysis	3.44 3.39	0.63 0.63	2.12 2.16	0.244	0.077 ....
Heat analysis	3.39 3.41	0.66 0.66	2.13 2.17	0.248	0.077 ....
Heat No. 749—Pig Iron Charge					
The charge was made up of two pigs from the same car lot. The analyses and weights of each pig were as follows:					
78 lb., pig No. 3, lot 14..	3.41 3.39	0.46 ...	3.31 3.29	0.110	0.048 ....
44 lb., pig No. 4, lot 14..	3.60 3.49	0.42 ...	3.25 3.24	0.114	0.045 ....
The estimated analysis of charge based on these analyses was.....	3.47	0.45	3.28	0.112	0.047 0.058
Actual analysis of heat.	3.56 3.61	0.46 ...	3.14 3.13	0.114	....
Heat No. 751—Pig Iron Charge					
This heat was made up in the same manner as heat No. 749.					
46 lb., pig No. 3, lot 13..	3.44 3.81	0.55 0.55	2.99 2.97	0.42	0.014 ....
49 lb., pig No. 4, lot 13..	3.78 3.60	... 0.55	3.55 3.57	0.036	0.014 ....
The estimated analysis of charge based on these analyses was	3.45	0.55	3.27	0.039	0.014
Actual analysis of heat.	3.42	...	3.24 3.22	0.022	0.023 ....
Heat No. 754					
This heat was made up in the same manner as heats 749 and 751.					
51.5 lb., pig No. 1, lot 13.	3.76 3.65	0.58 ...	2.96 2.97	0.048	0.006 ....
54.0 lb., pig No. 2, lot 13.	3.81 3.78	0.55 ...	3.55 3.57	0.036	0.014 ....
The estimated analysis of charge based on these analyses was	3.75	0.54	3.26	0.042	0.010
Actual analysis of heat.	3.69 3.62	0.55 ...	3.12 3.12	0.042	0.024 ....

excessive chemical losses in the melt. Oil on the borings will cause no more trouble than in the melting of oily brass or bronze turnings. The shrinkage of the iron produced from the melting of borings is no different from that in melting pig and scrap. This has been determined by making K-bars and castings of non-uniform section and comparing with similar castings made from pig and scrap melted in both electric furnace and cupola.

TABLE II.

Physical Tests of Electric Furnace Iron.

Heat	T. C.	Mn	Si	P	S	Load	Mod. of Rupture	Deflection
Borings								
151	3.21	0.50	2.46	0.58	0.098	*3460	54000	0.154
33	3.18	0.46	2.11	0.72	0.090	3220	50200	0.171
55	3.26	0.57	2.29	0.51	0.088	3330	52000	0.183
Pig and Back Scrap								
244	3.25	0.74	2.18	0.10	0.025	3280	51200	0.175
291	3.26	0.57	2.21	0.24	0.030	3370	52600	0.212
339	3.28	0.76	2.20	0.24	0.044	3300	51500	0.157
Back Scrap								
68	3.28	0.50	2.23	0.51	0.082	3610	56300	0.159
69	3.30	0.50	2.15	0.52	0.087	3370	52500	0.195
70	3.23	0.47	2.32	0.48	0.086	3420	53400	0.175

* Standard A. S. T. M. Test Bars.

Table II contains some comparative physical tests of iron produced from heats of borings, pig and back scrap, and all back scrap.

All these heats have been selected so that the iron has the same chemical analysis, and having been poured under the same conditions the values are strictly comparable. It would seem from

these results that under the melting conditions in this furnace, it makes no difference in the quality of the metal whether we are operating on pig or scrap, provided the chemical analyses are the same.

Table III records a few heats selected from our every day record. These results are selected to show the possibilities in the physical properties of irons melted in this furnace. The first five heats are made from pig and back scrap, to which 20 percent of steel has been added. The last five heats are made from pig, back scrap, 20 percent steel and 10 to 12 percent Mayari pig.

TABLE III.

Some Analyses of Electric Furnace Iron

Heat	T. C.	Mn	Si	P	S	Cr	Ni	Load	Modulus of Rupture	Def.
296	3.24	0.60	2.13	0.58	0.065	...	...	4440	69250	0.185
282	2.97	0.57	2.10	0.54	0.069	...	...	4680	73000	0.175
534	3.23	0.76	2.47	0.69	0.025	...	...	4250	66300	0.222
537	3.16	0.70	2.45	0.155	0.024	...	...	4350	67900	0.200
554	3.01	0.50	2.00	0.138	0.026	...	...	4680	73100	0.183
455	3.07	0.70	2.62	0.22	0.037	0.40	0.20	4480	69800	0.169
465	3.11	0.58	2.69	0.248	0.038	0.36	0.18	4520	70500	0.172
489	3.02	0.65	2.72	0.120	0.030	0.25	0.12	4570	71400	0.175
493	3.31	0.68	2.28	0.120	0.025	0.30	0.15	4460	69500	0.230
571	3.03	0.56	2.58	0.085	0.023	0.28	0.14	4640	72300	0.241

This furnace has been very satisfactory for our purpose. Whether or not it would be satisfactory in larger size, or under different conditions, we would not attempt to say. We believe that this type of furnace has a field in the melting and reclaiming of borings, in foundries which have a machine shop in connection. The furnace is well adapted for experimental work, and mixtures of any analysis can be handled. We have made synthetic iron from boiler punchings, ferro silicon and carbon; malleable from borings and steel; and alloy irons of various kinds. The furnace is adaptable to all types of melting where refining by slagging is not required.

DISCUSSION.

H. M. WILLIAMS: This was not put in as a production furnace, but simply to make some tests on cast iron for cylinder blocks. As soon as the furnace was installed, the model making department found that we could make castings and we have been busy with production ever since.

RICHARD MOLDENKE[2]: The results gotten from cast borings are very interesting. The difficulty in treating borings lies in the fact that there is an enormous surface going with a small weight; and the surface retains air in contact with it even when the particles are pressed together under heavy loads. This increases the difficulty in melting and adds oxidation troubles. If the borings can be kept from oxidizing in melting, considerable has been gained.

H. M. WILLIAMS: I might say that in melting pig and scrap, the first heat requires 175 Kw.H., the second heat 110 Kw.H., the third heat 105 Kw.H., and the fourth heat 100 Kw.H. The average heat charged is 250 to 280 lb. In melting borings, the first heat requires 170 Kw.H., the second heat 80 Kw.H., the third heat 70 Kw.H., and the fourth heat 70 Kw.H. The average heat charged is 250 to 280 lb.

G. K. ELLIOTT[3]: In regard to the picking up of sulphur, I can say that I have had similar experience with the same furnace and I learned to attribute the acquired sulphur to the cutting oils with which a part of the borings were freely covered, because many of these oils were found to be remarkably rich in sulphur.

H. M. WILLIAMS: I was referring to charges of pig iron not borings.

G. K. ELLIOTT: My reference was to heats of cast iron borings and the slight pick-up of sulphur that occurred could be explained only in this way.

ROBERT TURNBULL[4]: I would like to ask Mr. Williams whether he uses any coke at all or adds the charge without coke. I thought

[2] Consulting Metallurgist, Watchung, N. J.
[3] Chief Chemist and Met., The Lunkenheimer Co., Cincinnati, Ohio.
[4] Managing Director, U. S. Ferro Alloys Corp., Niagara Falls, N. Y.

if he added coke, this would be an explanation of the higher sulphur.

H. M. WILLIAMS: The charge is put in without coke and when any carbon is added, we use broken electrodes.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, Mr. Bradley Stoughton in the Chair.

ELECTRIC FURNACE IRON AND STEEL. INTERMITTENT AND ALTERNATING OPERATIONS.[1]

By W. E. Cahill.[2]

Abstract.

It is shown that in Treadwell, Alaska, cast iron is made more cheaply in the electric furnace than in the cupola. Analyses figures show that from charges of all-scrap cupola-melted iron the electric furnace produces metal of greatly reduced sulphur content. Factors affecting the economy of melting and the advantages of the electric furnace in foundry practice are discussed. The average power consumption for twenty-five consecutive heats of iron and steel, with a two-voltage control, shows a saving of 75 Kw. H. per ton of iron and 42 Kw. H. per ton of steel. The effects of intermittent operation on the furnace and the precautions necessary in alternating heats of iron and steel are discussed. [A. D. S.]

The Alaska Treadwell Gold Mining Company has been manufacturing electric furnace iron castings since October, 1918. This places them among the first, if not the first, to enter the field on a commercial basis. The factors that entered into the adoption of the electric furnace were many, and the results attained such as to warrant the discontinuing of cupola melting.

For a period of about seven months in the year the Treadwell Company has a surplus of electric power generated by their hydro-electric plants. During shortage power may be obtained from another local company at a very reasonable rate. Hence the factor of power supply which is most important is very

[1] Manuscript received January 27, 1922.

[2] Metallurgist and Foundry Superintendent, Alaska Treadwell Gold Mining Co., Treadwell, Alaska.

favorably taken care of. We are charged nominally at the rate of one cent per Kw. H. Connellsville coke costing $8 per ton on the Atlantic Coast costs $48 per ton delivered to the foundry. Foundry pig iron costs from $45 to $50 delivered. The conditions above mentioned make it possible to produce electric-furnace iron castings cheaper than can be done with the cupola, not to mention the great difference in quality.

TABLE I.

Heat No.	Si	Mn	S	P	C	Graph C
14A	2.15	0.44	0.030	0.334	2.96	...
149	2.02	0.47	0.056	0.49	2.90	...
13B	1.83	0.57	0.020	0.41	2.95	...
70	2.19	0.64	0.048	0.44	2.96	...
121	1.93	1.28	0.054	0.50	3.01[1]	...
144	1.88	0.61	0.064	0.37	3.17	...
151	2.19	0.67	0.044	0.45	3.23	...
154	1.64	0.63	0.031	0.40	3.23	...
163	0.69	0.54	0.071	0.23	2.50[2]	...
166A	0.69	0.49	0.086	0.190	2.43[2]	...
166B	1.78	0.55	0.032	0.195	2.42[3]	...
172	0.65	0.62	0.049	0.29	2.50[4]	...
178	2.18	0.58	0.031	0.36	2.55	2.54
181	2.00	0.54	0.027	0.38	2.80	2.81
184	1.56	0.58	0.023	0.195	3.27	...
1C	1.79	0.56	0.049	0.52	2.81	2.62
48	1.56	0.47	0.069	0.33	2.72	2.71
61	1.77	0.55	0.054	0.40	2.77	2.50
77	1.73	0.57	0.063	0.53	2.58	2.57
92	1.74	0.45	0.055	0.53	3.16	2.78

[1] After first tap 160 pounds manganese steel was added.
[2] Hard iron.
[3] Before last tap of 166-A 12 pounds ferro-silicon was added to pour a rush order of castings. These castings machined nicely.
[4] Add to anaylsis—Cr 0.61. Chrome ore was used in charge with gray iron to make hard iron.

It was soon found that pig iron was unnecessary. An all-scrap charge of machinery scrap melted and refined on a basic hearth resulted in a superior quality of metal. The melting is done in an 800 Kw., 3 phase, 2-ton Heroult furnace in a neutral or reducing atmosphere under a reducing slag. Refining takes place during the whole period of melting, and by the time the bath has been raised to the required pouring temperature the sulphur has been removed below all practical limits, and the metal is ready for the moulds.

For medium weight castings no additions are made; for small castings and thin sections the silicon can be increased as desired

by addition of the ferro-alloy. The analyses in Table I are mostly from all-scrap cupola-melted iron that has been through the electric furnace.

From the above table of analyses it is evident that one of the problems of iron foundry, *i. e.*, the high percentage of sulphur in commercial scrap, can be easily eliminated through the medium of the electric furnace. Phosphorus can be controlled by the use of steel scrap; silicon and manganese by the addition of the ferro-alloys to the bath.

For economic melting of cold scrap iron in the electric furnace the nature of the charge is very important. The charge must not be too dense, otherwise the electrodes will not penetrate the charge, but do most of the melting from the top. This will cause early heating of the upper part of the furnace with subsequent losses by radiation. The melt will be dead, and will require considerable unpleasant manual labor of poking to free the bottom of metal. Sprues and gates make the best charge for the bottom, clean scrap for the top is desirable for electrical conditions, as insulation is very common when melting cast iron. In starting very low current is used until a good circuit is established. If insulation develops, the best remedy is to shovel crushed electrodes, about walnut size, around the electrode that is giving trouble. This electrode material will afterwards unite with the lime to form a carbide slag. As soon as full current is on the lime is shoveled in. The lime requirements are about two percent of the charge, with sufficient fluorspar or silica sand added to make it active; coke is added with the lime. The resultant slag is strongly carbide and will analyze up to nearly one percent sulphur. If the slag is kept right, very little hearth repair is necessary, usually 10 to 20 pounds of magnesite will suffice. The danger of burning the bottom is slight, as cast iron melts at a much lower temperature than steel.

The temperature of the metal is under control of the operator. Electric furnace iron is necessarily poured hotter than cupola iron, due to the absence of fluid forming impurities. By running hot iron it is possible to reduce the size of gates and risers.

Foundry procedure when using an electric furnace is different from the cupola. The time-honored custom of moulding until the

cupola blast is on is discontinued. The pouring does not interfere with the moulding, the pouring being done by a few men. The rush to keep the metal away from the cupola no longer exists. The confusion of dull heats has gone. Iron from the electric furnace may be tapped in any amount from a few pounds to the whole charge and at any interval, the remainder in the furnace being held at the required temperature until called for, raised or lowered if desired. The floor can be cleaned up almost immediately, as low sulphur iron is noticeably not so tender, and may be pulled out while still hot without injury.

The most distinguishing characteristic of electric furnace gray iron is its uniformly fine-grained nature. It is claimed by some to be due to low phosphorus, which prevents grain growth. As the same texture is found when the phosphorus is fairly high, low sulphur must have some influence, but probably the greatest factor is the thoroughly deoxidized condition of the metal and the absence of occluded gases.

Power consumption varies greatly with both iron and steel, depending upon whether or not the charge is melted in a cold furnace or after a previous heat. During the spring of 1920 our transformer was wired to give two-voltage control, giving a range of 100 to 120 volts. While the range is not very great, the results are interesting.

	Iron Kw. H. per ton	Steel Kw. H. per ton
Single voltage	784	893
Dual voltage	709	851

The averages were taken for twenty-five consecutive heats each of iron and steel after new lining. With steel the higher voltage is used for melting and the lower for refining; with iron the change is made to lower voltage when the scrap is nearly all in. If the higher voltage is left on after the scrap is all in the furnace heats up too much. The above figures are for intermittent operation and may seem high, but melting cold scrap in a cold furnace is necessarily high, as considerable energy is absorbed in heating the furnace.

Intermittent operation of the electric furnace shows its most severe effect on electrodes and roof. During the period of idle-

ness the electrodes are above the oxidizing temperature for several hours, which causes the electrodes to pencil. The reduced area causes electrical resistance. The reduction continues until it cuts through to the thread and the stub (about 14 inches [35 cm.] average) drops off. Graphite electrodes should be more suitable for intermittent operation with favorable scrap conditions. For melting gray iron scrap the breakage might be prohibitive, as it frequently happens that all three electrodes will become insulated and the whole weight thrown directly upon them. In our three years of operation we have only broken two carbon electrodes, and these broke in the threads soon after the joint was made.

TABLE II

First heat of steel after iron

Si	0.15	0.34	0.39	0.24
Mn	0.68	0.87	0.57	0.58
S	0.052	0.048	0.049	0.068
P	0.065	0.040	0.048	0.047
C	0.41	0.50	0.31	0.37

Second heat of steel after iron

Si	0.27	0.32	0.34	0.31
Mn	0.73	0.68	0.78	0.79
P	0.038	0.041	0.041	0.018
S	0.021	0.026	0.030	0.040
C	0.40	0.47	0.34	0.42

Alternating heating and cooling of the roof, with its corresponding expansion and contraction, causes spalling of the silica brick. Sheet asbestos seems to be the best expansion medium. We have been able to get over 200 heats to a roof.

When alternating heats of iron and steel great care must be taken in furnace operation. Of prime importance is a good spout so that the furnace will completely drain. The effect of residual iron is very noticeable on steel. The slag must be fluid enough to run out with the iron, otherwise it will mean additional sulphur to be removed from the next heat of steel. If a heat of steel is desired after iron, the furnace should be charged with low carbon steel scrap so the melt will be fairly low. The carbon may be lowered by adding iron ore, but there is a limit to this reaction. If carried too far it will begin to show its effect on the

furnace. The removal of sulphur is not dependent upon carbon in the steel, but upon the length of time the steel is held under a carbide slag. If the sulphur is high the heat will necessarily be prolonged, which is objectionable for furnace reasons.

The analyses for steel directly after iron are shown in Table II.

After the first heat of steel there is no noticable effect of iron, and the procedure may continue as in ordinary practice.

DISCUSSION.

Bradley Stoughton[1]: It seems to me that this is one of the most economically important papers that we have had, because here is a case where there isn't any question that a man is making iron castings and steel castings in the same furnace at intervals at a less cost than he could make them by the standard methods. Of course, the reason for that is that he is way up in Alaska where pig iron is inordinately expensive, and where coke is not any too cheap; it is cheaper now since they have started that Anyox plant, but it has not been at all cheap, and he really can make his castings in the electric furnace at a lower price and a higher quality than he could by the cupola or the air furnace or the open hearth furnace, as the case might be. Now there are a great many places in the world where conditions like this prevail; we can set up an electric furnace and make an iron casting, if it is needed, or a steel casting. They can use the broken parts for a pattern, with a certain amount of modification and care, and they have a really practicable method of using the electric furnace as a great industrial asset to their plants.

Frank Hodson[2]: Mr. Cahill mentions the difficulties he experienced with getting electrodes to penetrate the charge and prevent melting from the top only. Mr. Brooke also brought out that important point in cast iron melting, having a furnace in which the melting is done from the top. Probably one reason why the small Booth furnace was so successful on iron was the washing of the borings thus aiding melting. I really think the

[1] Consulting Engineer, New York City.
[2] President, Electric Furnace Const. Co., Philadelphia, Pa.

furnace with a bottom connection or one with a combination where you can melt the charge down from the top during the first part of the heat and afterwards switch on the bottom electrode would be very desirable; if you can get circulation of any kind of the charge, you are going to cut down your energy input and get a much better quality product. I think the occlusion of gases and oxides of iron is one of the worst things we have to contend with. Mr. Cahill mentions that the fine grain nature of his electric furnace gray iron is probably due to low phosphorus. I think the discussion this morning brought out that it is more likely to be due to low sulphur and freedom from oxides and gases. The comparative results in terms of Kw.H., reduced and dual voltage, are very interesting to me. We made some tests a year ago on the same thing and we found practically identical results. Dual voltage is not as important as might appear. You can get similar results by reducing the input into the furnace probably with one voltage; at a certain stage of melting, the furnace charge cannot absorb the heat fast enough. Accordingly, if more power is being put into the furnace than is actually needed, dual voltage will correct that condition, but it is not due to dual voltage that you get the low Kw.H.

ROBERT TURNBULL[3]: I do not agree with Mr. Hodson about dual voltage; I believe it is a much superior method of melting to single voltage, and so far as absorbing the amount of power, I think the surface covered by the higher voltage arc is sufficient to absorb the amount of power which is put behind standard furnaces. This has been clearly shown in my own experience, where we found a difference of easily 30 percent in the output of the furnace with dual voltage as compared with single voltage.

FRANK HODSON: I do not mean to suggest that the dual voltage is better than the single voltage, but rather that it is not the only means of saving Kw.

G. K. ELLIOTT[4]: From Mr. Cahill's figures, we learn that his coke costs $48.00 a ton. Since a good average melting ratio of iron to coke is about 8 to 1, we find that it requires $6.00 worth of coke to melt one ton of iron. Again referring to Mr. Cahill's

[3] Managing Director, U. S. Ferro Alloys Corp., Niagara Falls, N. Y.
[4] Chief Chemist and Met., The Lunkenheimer Co., Cincinnati, Ohio.

figures we find that his current consumption ranges from 709 to 784 Kw.H. per ton of iron for which one cent per Kw.H. is charged, making the current cost for one ton of iron equal $7.09 to $7.84. This is to be compared with $6.00 for coke to melt one ton of iron. Herein we have illustrated the great cheapness of cupola melting in that it can melt iron with $48.00 coke more cheaply than the electric furnace can do it with electricity at one cent per Kw.H. Therefore we are forced to conclude that the saving Mr. Cahill has attained is not through the fuel, but must be through the substitution of cheap scrap in the place of pig iron.

Ernest Thum[5]: It may be interesting to call your attention to the fact that in the Sacramento shops of the Southern Pacific Railroad there is a furnace very similar to the furnace operating in Alaska which has done some rather remarkable work. They have made synthetic iron there, and iron and steel castings of a large number of different analyses. At the present time I believe they are working 24 hours a day on a large order of tie plates. The railroad has a small merchant mill in their general shops and the steel furnace is, therefore, casting a small ingot which can be broken down in their roughing train and rolled directly into bars from which the standard tie plates are made. Raw material is what is called wrought iron scrap, by railroad men; probably old tie plates, splice plates, bolts, rods and similar metal from the track and repair yards. It contains more low carbon steel than wrought iron. This steel furnace also makes from day to day any orders for steel castings, in fact supplying all steel castings for the entire railroad system, in a wide variety of castings. In manufacturing such things as locomotive frames for stock, they have introduced some very interesting methods which anyone who is working on electric steel castings would be very much interested in investigating. The problem in Sacramento is very similar to the problem in Alaska; that is, they have very high-priced coke and very high-priced pig iron, both of which rule out Bessemer converter steel on account of a high cupola melting cost. The open hearth was considered far less flexible for general utility work than the electric furnace, although the production cost was figured to be approximately the same.

[5] Assoc. Editor, Chem. and Met. Engineering, New York City.

W. E. Cahill (*Communicated*): As Mr. Stoughton stated, I think many isolated plants would find a small electric furnace installation a great asset in case of emergencies. Often a casting must necessarily be of steel, and that means unavoidable delay. Recently the front head of an all-steel jaw crusher broke. This casting weighed 11,000 pounds, and earliest possible delivery from the outside was ninety days. While this casting was beyond our capacity as a single piece, we were able to make it in five interlocking sections, and the crusher was working again in a short time. Over twenty years ago a small iron foundry was built at Treadwell to take care of "break downs." This developed until operations were more on the order of a commercial foundry. Our production now is about 500 tons of steel castings and 250 tons of iron castings per year.

Mr. Hodson's point is a good one. Bottom heating should prove helpful in melting gray iron. I am afraid Mr. Hodson failed to read completely the paragraph relating to the fine grained nature of electric furnace gray iron. His hypotheses are almost identical with those stated.

In regard to dual voltage, I agree with Mr. Turnbull. If nothing else, dual voltage permits of more flexibility. With gray iron it is necessary to change to the lower voltage sooner than with steel, as the shading effect of the scrap does not last as long. The rate at which the charge will absorb heat depends in a large measure on the condition of the slag.

Mr. Elliott is right, the use of an all-scrap charge makes the melting cost less. However, we have the power and an abundance of scrap. Pig iron and coke must be purchased from the outside and a large stock carried to insure continuity of operation. Coke and iron must be hoisted up to the charging floor of the cupola, while with the electric furnace the fuel comes by wire and the iron is trammed to the main floor only. In fact, so many points are involved that the real answer is the final cost of castings, which we have found to be much less.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, Mr. Bradley Stoughton in the Chair.

A COMPARISON BETWEEN SHAFT AND OPEN TOP FURNACES IN THE MANUFACTURE OF PIG IRON ELECTRICALLY FROM IRON ORE.[1]

By R. C. Gosrow[2]

Introduction.

The electric smelting of iron ore brings into consideration certain features of furnace design, which are peculiarly applicable to this art. When electric reduction of iron ores was initiated, the first furnaces were patterned after the iron blast furnace. The builders of these furnaces considered that stack reduction was an absolute certainty and necessity, and as a consequence the uni-shaft and the multi-shaft furnaces were developed.

STACK TYPES OF FURNACES

The necessity of the stack on an electric reduction furnace has never been absolutely settled. It is true however that for many years no furnaces were built without a stack, or a number of them. However with the development of the art, the stack type of furnace developed into an open top furnace, eliminating the stacks.

In the circular as well as the rectangular types of stack furnaces, incompatibilities in proportioning the stacks and the crucible were apparent. The commercial 1500 Kw. furnace measured about six feet to eight feet (182 to 243 cm.) in crucible diameter, with a forty-eight inch (121 cm.) diameter stack, twenty-five to thirty feet (7.6 to 9.1 m.) high. The rectangular furnace with the same electrical capacity, was about twenty feet (6.1 m.) long, by eight feet, (243 cm.) and ten feet (3 m.) deep, with four or five stacks ten to twenty feet (3 to 6 m.) high, and

[1] Manuscript received February 18, 1922.
[2] Consulting Electrometallurgist, Buffalo, N. Y.

three feet (90 cm.) diameter up to three by five feet (90 by 150 cm.) in area. On these furnaces, the rate of feed, and the quantity of material charged to each varied greatly. This would give ratios, of crucible to stack in the circular furnace of 3.08 to 1; in the rectangular furnace with circular stacks 4.55 to 1, and with retangular stacks 2.14 to 1. From these figures it is apparent that the work the same electrical energy must perform would also vary greatly. As no more material could be smelted, than what could pass through the feed stacks, less material was actually smelted. This is accounted for by the fact that the stacks were constantly frozen up with the charge, which fused by contact with the hot exit gases.

Attempting to eliminate the difficulty arising from frozen stacks, smaller stacks were used, but the charge fused more quickly and the trouble was intensified.

In consideration of experience with stack type furnaces, it would seem that by making the stacks higher, and of such cross section that fusing of the charge would not completely close the stack, the difficulty would be overcome. It must be considered however in making such a recommendation, that the height of the stack is dependent on the conditions in the smelting zone of the furnace. In furnaces of large electrical capacity, large carbon electrodes are required, so that their mechanical strength allows greater loads to press against them. without fracture. If only the electrode were the subject of consideration, it might be assumed that with large electrodes large stacks may be used, and vice versa. This is not true. At no time in the history of electric iron ore reduction has the electric furnace approached the stages of masterful manipulation reached by the iron blast furnace. Hangups and slips in the iron blast furnace take place with no apparent damage to other equipment. A hangup followed by a slip in the electric furnace, usually means breakage of one or more electrodes, contributing to electrical disturbances, which often result in days and even weeks of delay. In the electric reduction furnace, after a delay, the load is not at once established by the closing of the switch.

The purpose of the stacks in either the uni- or the multi-shaft furnaces, was to prepare the charge for the smelting zone of the furnace by preheating it, and also to distribute it evenly at or near

the electrodes, by virtue of the position of the stacks and their shape. The necessity of uniform feed and distribution is realized, and the balance required between the feeding and the smelting zones of the furnace. As the charge has a long travel from the top of the stack to the smelting zone at the electrode ends, the time for the size of the ingredients to become smaller and to segregate is sufficient to upset any nice conditions originally present, while feeding the charge. Also any air leaks which may occur in the stack construction will dissipate carbon, required for reduction when the charge reaches the reducing zone. The condition of the charge when mixed, or charged to the charging device on the feed floor, is at least thirty feet from the zone where all the ingredients become fused for separation. Also as the operation of the electric furnace depends on the charge for the generation and propagation of heat for smelting, it is essential that this condition be considered primarily, as without heat no smelting takes place. In the shaft type furnace, the completely enclosed furnace interferes with any direct indication of what conditions inside of it may be. The accuracy of determining the height of the charge, or the position of the electrodes is most difficult.

Advocates of the shaft type furnace contend that for wet ores, the shaft preheats and dries the ore. They also assert that for carbonate ores, calcining takes place, expelling CO_2 gas, constituting a saving in heat. This it does. They contend that reduction is accelerated by the use of the stacks. This I believe remains to be proved. In the electric reduction furnace the direct-carbon-to-ore-contact at the temperature of the reducing zone, makes the reaction complete. While the reduction of ferric oxide to ferrous oxide is a step reaction, yet the velocity of the reaction is such that the reduction of the ferric oxide to iron is complete, with the step reaction practically eliminated. The utilization of the furnace gases has been resorted to for cooling the crucible roof, and also for other metallurgical operations. The stack furnace provides means for the collection of the furnace gases, with the minimum amount of air. In the stack furnace the ratio of carbon dioxide to carbon monoxide will vary with operations. As a source of metallurgical heat this gas will be uncertain in its heat units. If carbon is oxidized to CO_2, and the gases are low in heating constituent, then their fuel use is low. If they are high in

CO, because of carbon being oxidized to CO, their efficiency as a reducing material is high. The advantage of stack reduction may be more fully realized, when the correct equilibrium of conditions is maintained. I would say that stack constructed furnaces operate better on magnetite ores, using some more refractory and stronger reducing material than charcoal.

In feeding the stack furnace, the method of feed must be appreciated, in its relation to the rate of smelting the burden. All reduction is accomplished by carbon, or carbon monoxide gas. The feed is by a choke method, comparable to the choke feed in roll crushing. Unless the smelting of the charge can cause a shrinkage in the volume of it, no more material can be let down through the stacks. At the base of every stack there is exerted on the charge below it, a pressure equal to the weight of the charge in the stack. The effect of this pressure is to interfere with the conductance and the resistance of the charge at the electrode end region. In a charge consisting of a considerable volume of charcoal, the crushing of the charge on the charcoal, at once upsets the resistance of the charge as originally anticipated. And as the function of the charge is to provide a resistor and a conductor for the current brought into it, from the electrodes, it is of extreme importance that this be first considered in the smelting furnace. Another condition may also be cited.

With the charge pressure from each stack as a constant on the lower levels of the crucible contents, any bridge which may form over the fused and molten cavity below, will have to support this charge. Ultimately this charge must drop. When this occurs the abrupt entry of cold unfused material into the incandescent zone, at once causes a drop in the electrical load and the furnace "goes off." This condition is generally a result of tapping slag or metal. The reason for the crust or bridge forming, is because no means are at hand to prevent it, with the closed in furnace. With a furnace in which air blast is forced into the cellular structure of the carbon bearing material, the effect of packing of the charge has no effect on the propagation of heat. But in the electric reduction furnace packing of the charge so changes the electrical property of the charge, that with all reducing materials the effect will not be the same.

Furnaces with superimposed stack construction of course

require a larger capital expenditure. This is consumed in the heavier shell required, more overhead carrying structure for the stacks, and gas outlet apparatus and piping, and the refractory linings for the stacks. With stack construction arches are required to close in the spaces between the stacks, requiring high grade refractory materials for this use. With the circular shaft furnace, special brick shapes are needed for the domed roof, which is considerably weakened by the entry of the electrodes through it.

OPEN TOP TYPE OF FURNACE

In discussing this type of furnace, a question might be asked, viz.: If the raw materials can be charged to the furnace at a sufficient rate, and reduction can be accomplished by ore and carbon contact, producing marketable iron, wherein is the necessity for stacks? This question may be answered by asserting that they are not necessary.

Let us consider the reactions in the furnace, resulting in the production of the iron. The reactions are dependent on the quantities of the reacting materials present, and the temperature at which they react. They also depend on how the electrometallurgist interprets and considers them. He may desire to consider his carbon as being oxidized to CO_2, or he may consider it as being oxidized to CO. If he considers CO as the resultant gas, he would naturally consider the reducing power which this gas possesses, and provide for its use. In using it he would most likely bring it in contact with raw ore, and allow some reduction to take place. If he considers the carbon forming CO_2, he has a gas which has no reducing power, and consequently he will provide for its release as soon as free.

With the calculation of carbon for reduction, as forming CO, twice the amount is necessary as when the calculation is made for carbon to form CO_2. As the efficiency of the electric reduction process depends on the economies practiced in smelting the burden, this conservation of carbon is worthy. The reactions for direct reduction would be essentially these:

Carbon forming CO_2—

$$2Fe_2O_3 + 3C = 4Fe + 3CO_2 \qquad (1)$$

Carbon forming CO—

$$Fe_2O_3 + 3C = 2Fe + 3CO \qquad (2)$$

In reaction (1) twice the amount of ferric oxide is reduced with the same amount of carbon as in reaction (2). In the highly heated smelting zone of the electric furnace, direct carbon reduction to iron takes place. The minimum amount of carbon accomplishes the reduction, plus the necessary amount for carburization of the iron, occurring in either case.

With the open top furnace, the charge has a shorter travel. Results show that this shorter travel has many benefits, in increased rate in the smelting of the burden; elimination of delays incident to stack feeding; freedom in working the charge by stoking to prevent crusting and hangups; accurate control of the product on account of the shorter time for the material to pass through the furnace; accurate knowledge at all times of the height of the charge and the position of the electrodes; a decreased initial cost of the furnace.

As the electrical conditions, to promote smelting, are dependent on the density of the charge and the size of ingredients, the distribution of the carbon material in the charge, the temperature at which the material enters the zone of reduction and smelting, it is reasonable to contend that if the material can be charged into the furnace eight to ten feet from the zone of reduction and smelting, instead of thirty feet from it, the materials are in a better condition for electric smelting, as regards size of particles, mixing and distribution. The carbon material is not crushed by a heavy weight of overburden, nor is the charge packed.

The electric furnace is not a gas producer. Large volumes of air are not included in the reactions. With a properly operated furnace the gases leave the top of the charge at low pressure, and combustible gases burn freely, with a short flame.

As there are no stacks through which to feed the charge another system must be used. The most satisfactory type of feed mechanism has been the over-hung trolley hoppered-spout. This hopper has a flexible spout, from which the charge may be distributed to the exact spot or area desired in feeding. The labor is no greater than with the stack furnace, requiring much extra labor for barring down the stacks, and the feed hoppered-spout eliminates one crew of furnace hands. The trolley runs parallel to the furnace along one or both sides, and the hopper is filled from

the bins above. The charge falls on the top of the charge in the furnace, with slight impact, and packing is prevented.

The rate of feeding the charge is carefully controlled. The input of materials should be in the same ratio as the tapping of slag and metal. Feeding and tapping can be synchronized. Furnace practice often becomes slouchy. The furnace is allowed to run down, and then filled up rapidly. With the stack furnace this is possible. With the open top furnace this is not possible. The top of the charge is in full sight of the furnace crew, and it is soon apparent that continuous small charges are conducive to better conditions than few heavy charges. This is one of the main advantages of the open top furnace, the constant feeding of small charges, properly placed and distributed.

In considering the open top furnace, both the circular and the rectangular furnace are considered. Volume for volume and kilowatt for kilowatt of energy put into them, the rectangular furnace appears to be the better smelter. In the circular furnace the tapping of the metal and slag brings the heat to that point in the furnace towards the tap hole. In the circular furnace the electrodes are arranged on the points of a triangle, so that by causing the metal and slag to be drawn to the same point, the greatest heat is developed between those electrodes adjacent to the tapping notches. With the rectangular furnace the electrodes are in a straight line, on the center line of the furnace. The slag and iron notches are located in the long walls of the furnace. In tapping iron and slag, the location of the notches causes the heat to be centered, at or near the center of the furnace, at the middle electrode in straight three-phase three-electrode furnaces and at the two center electrodes in furnaces using split *delta* arrangement. This arrangement protects the end walls, and keeps the heat in the middle of the furnace. In the operation of the rectangular furnace, the end electrodes are kept higher than the middle one, or two.

The accumulation of accretions and sows in the electric furnace is something to be considered, and their removal provided for. In the open top furnace this is easily accomplished. The furnace can be run down very quickly, fluxing charges added, and the crusts cut out efficiently without any guess work.

The effect of the open top type of furnace on refractories is noticeable. The control of the charge and the distribution of it, has considerable to do with the maintenance of side wall linings. Side walls usually burn out, by the dead charge packing against them, and the hot gases heating the pack. The bricks are fluxed or the walls are damaged by barring. In this type of furnace the charge can be kept moving on the walls, and by constantly keeping new charge against them, the heat in the walls is given up to the charge in contact with them. By water cooling sprays on the jacket plates, burning out of wall brick may also be prevented.

One argument against the open top furnace for iron, has been the loss of carbon by the exposure of the charge to air. By properly feeding the charge this is avoided. Carbon charges may always be covered with ore or flux charges, or the charge may be mixed, and part of the ore charge added as a cover.

In the reduction furnace for iron, a well must be provided for the accumulation of the metal. The metal well should not have a holding capacity greater than four hour taps. The reason for this is that the current should not be given the opportunity to follow the metal path for too long a period. If a freeze up should occur, it is more quickly discovered and rectified in the open top furnace than in the enclosed shaft furnace. The formation of a crust along the top of the furnace is at once apparent by the heating of the electrode between the crust and the electrode holder. The rapid rise in temperature of the electrode is quickly noticed in this type furnace, preventing excessive oxidation and electrode consumption. From the standpoint of electrode breakage the open top furnace is a hundred percent an advantage. From the standpoint of labor required to operate this furnace it is about the same as the shaft type furnace, with the exception, that labor for barring down shafts is not required on this furnace.

In its simplest form the open top furnace represents a refractory lined steel shell with no covering arches or superimposed feed stacks. The initial cost of construction for labor and materials is the lowest and the cost of maintenance is also the lowest. The open top type of furnace for iron smelting has not generally been adopted. This is largely accounted for by the dominating position which the iron blast furnace holds in iron metallurgy, and

the close adherence to this pattern which electrometallurgists have practiced. I believe however, that with large units of seven to ten thousand kilowatts capacity, the open top furnace will be the practical unit. My reason for this belief is that smaller sized units will not be economical, and also that the large sized units will allow for construction features favorable to the open top furnace.

COMBINATION OPEN STACK TYPE OF FURNACE

This type of furnace is not a distinct type. It rather was designed to eliminate the troublesome arches, which were set between stacks, and also to utilize the vertical stacks for the dropping of the charge. In this furnace the whole top was open, as in the open top type, but the superimposed stacks hung about three feet from the charge.

In operating this furnace, the top of the charge was kept below the electrode holders, and level with the jacket side plates. There was no choke feeding of the charge, but free feed was adopted. The charge was dropped free through the stacks, and the impact of the falling material on the charge below, caused considerable packing, and crushing of the carbon material.

The essential difficulty with this pseudo-open top furnace was the feeding of the charge. I think it will be worth while to enumerate and mention some of the peculiarities incident with this furnace. When the open top was adopted, the lining was taken from the stacks, and the shell only remained. The charges were dropped all mixed, ore, charcoal and flux. It was observed that sufficient segration took place in a 15-foot (4.5 m.) drop, so that all the ore fell first and the charcoal was always on top of it. This of course caused much charcoal to be burned, unless light ore charges were added as a cover. But when the charges were not mixed and the charcoal charged first, the impact of the ore and flux falling on top of it, crushed the charcoal, so that instead of lump material as was desired, the result was fine material which would not have been charged initially. In order to eliminate this condition, baffle plates were set in the stack, so as to break the fall of the material. This further segregated the heavy and the light material, so that it was necessary to abandon this. The result

was that all ore or all carbon would find its position immediately around an electrode, upsetting all furnace conditions electrically. In order to place the charge as desired and absolutely essential to the running of the furnace, the hopper spout was developed. It might be said that this pseudo-type furnace was a transition between the stack closed furnace, and the open top stackless furnace.

FURNACE ELECTRODES

While the relative advantages of the two types of furnaces are not dependent on the type of electrode used, it seems fitting that a brief discussion of electrodes should be included in this paper. The two types of electrodes are covered by the plain carbon, and the graphitized carbon. A choice of electrodes should be made after a consideration of the items of first cost, service, mechanical strength, and electrical conductivity.

Relative to the first cost, an example based on 1914 prices with an open top furnace, will not be misleading, as the relative costs of the two are about the same.

Furnace load 1800 Kw., 60 volts across the phase, 3-phase furnace, 4 electrodes, 140 in. (3.6 m.) necessary per electrode string. Based on 17,000 amperes per terminal, with the end electrodes each carrying more than half this amount.

Plain Carbon

Cross section to carry load	285 sq. in.	
140-inch length, required weight	1900 lb.	
Four electrode columns	7600 lb.	
At 7.5 cents per lb.		$570.00

Graphitized Carbon

Cross section to carry load	114 sq. in.	
140-inch length, required weight	740 lb.	
Four electrode columns	2960 lb.	
At 15.5 cents per lb.		458.00
Difference in favor of graphitized carbon		$112.00

As to service for smelting operations the two types compare about equally. As the graphitized material allows a better joint, on account of its machining properties, this would be an

advantage in preventing joint oxidation and weakening of the joint. The greater heat conductivity of the graphite electrode promotes better cooling of the electrode in the holder contact. But the cooling area of the graphite electrode is less than that of the carbon electrode, so that the charge around the electrode would take up more heat from the carbon electrode than from the graphite electrode. It is the cooling of the electrode which promotes its useful life. The graphite electrode oxidizes at a much higher temperature than the carbon electrode, so this property would mean longer life.

Mechanically the graphitized electrode has greater strength for equivalent cross section. Electrically the graphitized electrode has three times the current carrying capacity.

The effective heating areas of the graphite electrode I have discussed in Chemical and Metallurgical Engineering, 1919, pages 235-241, in my article "Design of Electric Furnaces." The thermal influence of the carbon electrode would be about 1.6.

FURNACE AND PLANT COST ESTIMATES

In 1913 a furnace capable of producing 30 tons (27 metric tons) of pig daily, with transformers, charging mechanism, ore bins, building, cranes, electrical instruments, etc., cost about $50,000.

In 1920, a plant estimated to produce 20,000 tons (18,144 metric tons) of pig annually, and including all buildings, furnace equipment, transformers, instruments and wiring, charging machinery and cranes, the estimated cost is $750,000. In the ton-a-year cost average, this would amount to $37.50. In the 1913 furnace the total cost of plant would be about $150,000, or a ton-a-year cost of $16.66. The later plant was designed to employ every labor saving device, to decrease the operating cost, although the capital cost was greater. The plant was to be located in a settled manufacturing district.

PRODUCTION COST ESTIMATE PER TON OF IRON

This estimate is based on 1920 conditions in the western United States for a 20,000-ton-a-year plant, smelting magnetite and hematite ores, with charcoal and coke both available.

Item:	Unit Cost	Cost per 20,000 tons
Iron ore (at the smelter)	$ 4.00 ton	$140,000
Lime rock	2.00 ton	30,000
Coke	7.50 ton	60,000
Fluorspar	25.00 ton	2,500
Power (6750 KW-years)	30.00 KW-year	202,500
Furnace refractories, clay		9,000
Electrodes (graphitized)		100,000
Arcing carbons		4,500
Power and lighting for plant and motors		1,200
Stores and supplies		10,000
Labor—Furnace and iron production		60,000
Labor—Management, Superintendence, Metallurgical and Chemical Divisions		25,000
Labor—General plant, and non-productive		9,000
Interest at 7 percent		52,500
Depreciation, 5 percent annually		37,500
Amortization, 5 percent annually		37,500
Taxes and insurance		12,000
Total per 20,000 net tons		$793,200
Average cost per net ton		$ 39.66

This estimate does not take into consideration any market risks on the product in transit, or storage, nor interest on ore or raw materials in storage. It is considered that before the close of 1922 labor prices will be lower than those on which the estimate is based.

DISCUSSION.

Frank Hodson[1]: In reading over this paper I cannot help wondering with all the disadvantages of the closed shaft furnace, why it is that 98 percent of all the melting furnaces are of the closed shaft type? I think there are over thirty of those shaft furnaces now operating, and I do not know of a single open top furnace now operating. I would like the author to give his views on this.

[1] President Electric Furnace Const. Co., Philadelphia, Pa.

F. A. J. FitzGerald[2]: The results obtained with the Swedish furnaces do not show the economies that I believe were expected. The earliest experiments on making cast iron from ore were by Héroult at Sault Ste. Marie and so far as I have seen, none of the shaft furnaces have been any improvement over those experiments. Mr. Gosrow's figures show a consumption of 6750 Kw. years for making 20,000 net tons, which is equivalent to nearly 3000 Kw. hours per ton. This does not seem a good result. He also states that $100,000 worth of electrodes would be used for making this amount of iron. He does not give the price per pound of the electrodes but in another part of the paper he refers to 15.5 cents. Combining these figures this shows a consumption of 32 pounds of graphitized electrodes per ton. The consumption of 32 pounds of graphitized electrodes for 3000 Kw. hours of energy seems to be poor practice. It is not quite clear what the current density in the electrodes is. On page 118 he says 17,000 amperes are used per terminal. This may mean 17,000 amperes were carried by 285 square inches cross section of amorphous carbon electrode, say 60 amperes per square inch. If 60 amperes per square inch of amorphous carbon electrode are used, there is bound to be excessive electrode consumption.

Walter Graham[3] (*Communicated*): What information is available in reference to the manufacture of pig iron electrically from the Minette iron ore of Lorraine?

In view of the fact that France controls these ores and has important potential hydro-electric power in the French Alps and has little coking coal of usable quality, the Saar basin coal being of such inferior quality that Westphalian coking coal was always, prior to the war, used with it, this is a very interesting subject. France might surpass England and European countries generally in steel manufacture if the Lorraine ores could be smelted electrically.

D. A. Lyon[4]: In speaking of the use of the electric furnace for the production of pig-iron we should remember, as I understand it,

[2] Consulting Engineer, Niagara Falls, N. Y.

[3] Scientific Associate, Research Information Service, National Research Council, Washington, D. C.

[4] Metallurgist, Bureau of Mines, Washington, D. C.

that in Sweden it is really not pig-iron that is produced. I was talking this morning with Mr. Von Freesen and asked him "Are you really producing pig-iron or the hybrid metal which is suitable for making steel"? He replied, "We are still producing the hybrid metal." Therefore, I am of the opinion that in Sweden they are not producing a metal that is suitable for foundry purposes, but for steel.

As regards the open type of furnace versus the closed type: It has been my experience that a workman has to be a sort of a salamander to work around an open furnace. When you consider the amount of energy put into a large electric furnace, and the amount of gases given off and burned in the open type of furnace, you can easily imagine that to work around an open type of furnace is not very comfortable. I think probably the Swedish metallurgists prefer the closed type of furnace because of the ease of operation. If any of you have been down to Anniston and have seen Mr. Swan's furnaces working, you will get some idea, even in a semi-enclosed furnace, of the amount of gas that is given off and how hot it is around the furnace.

On the other hand, certain difficulties are encountered in operating the Swedish type of furnace. One of these difficulties used to be the melting down of the roof of the crucible, but I am informed that they have practically gotten away from that difficulty. Nevertheless, one wonders why, if the Swedish furnace is so satisfactory in its operations, it is not more generally used.

Mention has been made of the influence the blast furnace has had on the design of the electric shaft furnace. As we all know metallurgists are very conservative. The idea of the shaft furnace, as I understand it, is this; it was hoped to obtain reduction of the ore in the shaft. When I was at Trollhättan, they had all sorts of instruments for measuring the temperature in the shaft of the furnace, but I never observed a recorded temperature sufficient to effect reduction of the ore in the shaft before it got down to the crucible. The shaft may act as a pre-heater but I do not believe there is very much reduction of the ore in the shaft. As you know, circulation of the gases has been tried but I have never

learned that this has brought about reduction of the ore in the shaft. I think the principal benefit derived from the circulation of the gas is the cooling of the roof.

ROBERT TURNBULL[5]: I am going to invite Mr. Lyon to Niagara Falls and let him see some furnaces of 20,000 H.P. capacity, which men prefer to work around to digging trenches in the streets. The troubles mostly experienced with such furnaces are mainly caused by a lack of knowledge of how to operate them. Take a ferro-silicon furnace, as an example. During the war quite a number of new plants were started. I know of one in the Province of Quebec, Canada, where they were never able to operate their furnaces properly. They were nothing but Bunsen burners, and the men could not get near them to keep the charge in proper condition. Electrode holders were burned out, electrodes constantly breaking, and the owners lost about three times the amount of capital they put into the business. A properly operated open type electric furnace has no more inconveniences than the ordinary crucible furnace, perhaps fewer, as the handling of the crucibles when pouring the steel is a hotter operation than the charging and handling of an electric furnace. I think the main reason why shaft furnaces are being used in Sweden, is that they adopted this type and in consequence never gave the open type furnace a chance. After the experiments at the Soo, we designed a shaft furnace with electrodes on the side, applied for a patent, but never pushed it through, as we afterwards decided there was nothing to it. A Mr. Nystrom, who is a Swede, and who assisted at the experiments at the Soo, was of the opinion that the shaft furnace was all right, and when he returned to Sweden, he applied himself specially to the perfecting of that type of furnace. Mr. Lyon made a correct statement when he said that no high carbon pig was made in the shaft furnace. Very little else has been made but white iron, which is suitable for the manufacture of basic open hearth steel. If we wish to make all grades of pig iron, we must have a furnace that will do this. Whether the open top furnace would be satisfactory, I do not know. It is a pity Mr. Gosrow

[5] Managing Director, U. S. Ferro Alloys Corp., Niagara Falls, N. Y.

is not here to explain further the claims he makes in his paper. With regard to the paper itself, I have not much to say. I think it is an interesting one, but the suggested plant he mentions I think has been over-estimated in regard to capital necessary. Taking his costs here, with interest at 7 percent, depreciation and amortization, the yearly burden from these items would total about $125,000 to $130,000, whereas his total expenses for labor, management, superintendence, metallurgical and chemical divisions, only amounts to $85,000. There is something very far wrong in the cost of a plant of this description, where the items of interest, depreciation and amortization are nearly double the total operating costs. His figure is $750,000, and I feel certain the plant, as planned, could be built for $300,000.

Frank Hodson: I must take issue with Messrs. Lyon and Turnbull, for I have seen white and mottled iron made in Swedish furnaces, and I believe the reason they are not making mottled iron now is that it is more profitable to make white iron. They are using white iron directly in open hearth furnaces and they have found, strange to say, that it does not cut the furnace lining. In the reduction of iron and sponge, I think the experiments go to show that, even at low temperatures, there is considerable reduction. Taking the charges underneath the arch of the roof and through the furnace shaft proper will not only cool the arch, but will bring about partial reduction.

Robert Turnbull: As there is no silicon, or practically none, there is nothing to cut the furnace with.

D. A. Lyon: I have seen splendid gray iron made in an electric shaft furnace but the difficulty was to produce gray iron right along.

It is difficult in a shaft furnace to properly balance the charge, due to wet ores, difference in composition in charcoal or coke, etc. In a blast furnace the excess of coke simply means a hotter furnace, but in the electric furnace the effect is just the opposite, for there is nothing to consume the carbon except the oxygen of the ore; hence, with an excess of carbon the resistance to the

path of the electric current in the charge decreases, which means a decrease in temperature and the result is a cold furnace. Therefore, for reasons above stated, it was my experience that in a shaft furnace it is difficult to control the product; you may get gray iron, or you may get white; we got more white iron than gray iron. In Sweden the shaft furnace gives them the product which they desire. However, I am of the opinion that so far as the control of the furnace is concerned, that the open top furnace permits of the product of the furnace being more easily controlled than does the shaft type of a furnace. If a product is desired suitable for steel making, then the shaft furnace is all right.

FRANK HODSON: The control of the casting has a great deal of influence as to whether the iron is gray or white.

D. A. LYON: We always cast it the same way.

ACHESON SMITH[6]: Is not that the reason of all trouble they had with the Héroult?

D. A. LYON: Absolutely. When we learned of these reports that Swedish furnaces were so successful, I said "If they are so successful in Sweden, why aren't they in the United States"? I took a trip to Sweden and was not there ten minutes until I saw the answer; they were not making foundry iron at all, but metal for steel purposes.

ROBERT TURNBULL: I would like to say that at the Soo we never made a pound of white iron, it all contained from 3 to 4 percent of carbon, and this with an open furnace.

FRANK HODSON: As Mr. Lyon says, in nine cases out of ten they are not trying to make gray iron, they are trying to make white iron.

A MEMBER: May I add that in the plant that is being built in Brazil, which is designed by a very intelligent Swedish engineer, there will be, in addition to two of their latest type of shaft furnaces, an electric furnace which they intend to use as a standby.

[6] Vice-Pres. and Gen. Mgr., Acheson Graphite Co., Niagara Falls, N. Y.

In case some taps of pig iron are not hot enough, or are too low in silicon to blow, they will put it in an ordinary electric steel furnace and either increase the temperature, add ferro-silicon, or doctor it up in some way so that they can go ahead with making steel. Perhaps there is a little more uncertainty in the nature of the operation of the Swedish furnace. Even our best blast furnaces do not always give us the exact kind of iron we are after.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 27, 1922, Mr. Bradley Stoughton in the Chair.

THE ELECTRIC FURNACE IN THE IRON FOUNDRY.

A Bibliography.[1]

By Lyman C. Judson[2] and Harry P. Martin.[3]

The following list has been prepared with the thought that it will be helpful to those interested in the use of the electric furnace for the manufacture of foundry iron, if they wish to read further on the subject. Most of the articles have appeared in the past five years, as nearly all of the writing on the subject has been done in that period. The compilers have endeavored to make the list as complete as possible up to the end of 1921, but have confined it to articles concerning the production of iron for the foundry, and have excluded all articles relating to the separate field of iron smelting, as the latter has been well covered before.

1913.

Scott, E. K. Electric furnaces in iron and brass foundries. 1913. Foundry, **41**, 379-81.

General discussion of induction and resistance furnaces, and of the advantages which the Hering furnace possesses which make it adapted to the brass and iron foundry work.

1917.

Cone, E. F. High grade pig iron from scrap steel. 1917. Iron Age, **100**, 845.

Description of operations carried on by Sweetser-Bainbridge Metal Alloy Corporation of Watervliet, N. Y., with two five-ton Ludlum electric furnaces. Includes discussion

[1] Manuscript received April 4, 1922.

[2] Asst. Sales Manager, Acheson Graphite Co., Niagara Falls, N. Y.

[3] Export Manager, Acheson Graphite Co., Niagara Falls, N. Y.

of the metallurgy of the process, composition and properties of the iron, the question of cost, and the Ludlum furnace and its claims, 6 plates showing furnace in operation, diagrams of furnace.

Melting malleable iron in electric furnace. 1917. Foundry **45**, 140.

Patented process of W. G. Kranz, assigned to National Malleable Castings Co.

Pig iron from scrap steel. 1917. Min. and Sci. Press, **115**, 936-8.

Metallurgical features of process in Ludlum electric furnace used by Sweetser-Bainbridge Metal Alloy Corporation of Watervliet, N. Y.

Sawhill, R. V. Turning out pig iron from scrap. 1917. Iron Trade Rev. **61**, 437-43; Foundry, **45**, 399-405.

Details of process used at Ludlum steel plant, Watervliet, N. Y., with arc type three-electrode Ludlum furnace to produce low phosphorus pig, washed metal, cast iron and tool steel from all-scrap mixtures. Thirteen figures.

Turnbull, R. Electric pig iron in war times. 1917. Trans. Am. Electrochem. Soc., **32**, 119-123; disc. 123-127.

Discusses the influence of war-time condition on electric pig iron production, describes the furnace at St. Catherines, 6-ton, 3-phase, using 700 Kw. with daily output of 20 tons and manufacturing low phosphorus pig iron by melting steel scrap. Gives an analysis of iron produced.

1919.

Elliott, G. K. Electric furnace an adjunct to cupola. 1919. Amer. Foundrymen's Assn., 1919; Abstr. in Iron Trade Review, **65**, 891-2; Foundry, **47**, 687.

Describes a duplex process in which the preheating and fusion are done in the cupola, and the superheating in the electric furnace. Discusses advantages of such superheating.

Elliott, G. K. Improving the quality of grey iron castings by the electric furnace. 1919. Trans. Am. Electrochem. Soc., **35**, 175; Abst., Iron Age, **103**, 939; Foundry, **47**, 585.

Proposes to use a basic lined arc electric furnace to take grey iron from the cupola to refine and superheat it for special purposes. Experiments over a period of nearly two years show that electric furnace used in tandem with cupola, corrects the deficiencies of the latter, particularly as regards carbon regulation, conservation of alloying metals and refining.

Escard, J. Fabrication, proprietes et utilsation industrielle du fer electrolytique. 1919. Gen. Civil, **39**, 165-71, 225.

Reviews industrial processes of iron manufacture by means of electric furnaces. Points out best conditions in electric iron production. Properties of electric iron; composition is given in tables. Micrographs show structure of electric iron.

Gosrow, R. C. Castings from the electric furnace. 1919. Foundry, **47**, 858-62; also Iron Tr. Rev. **65**, 1706-10.

Flexibility of furnace recommends it to jobbing foundry as well as to large manufacturers. Discusses duplexing method for a steel foundry called upon to make large steel castings. Use of electric furnace for making grey iron castings.

Merrick, A. W. Refining of cupola malleable iron in the electric furnace. 1919. American Foundrymen's Assn. Sept., 1919.

Results of the experiments on the duplex process of melting malleable cast iron using a cupola and electric furnace. Effect in reducing sulphur and the influences of manganese. In one experiment material charged showed 0.20 percent sulphur, while sample 15 minutes later showed sulphur reduced to 0.057 percent. Author believes iron of any carbon and silicon desired can be made by proper additions of steel and ferro silicon to the bath.

Stock, G. J. Grey iron. 1919. Brit. Pat. 143,596; Chem. Abstr. **14**, 2909.

Production of grey iron in two stages, a white iron first obtained by smelting at 1200-1300° C., and the product refined in an electric or other furnace at 1500° C., with addition of carbon and silicon. If smelted in an electric furnace, the white iron contains 2 percent carbon, 0.5 percent silicon, and 0.3 percent sulphur; the refined product contains 3 percent carbon and 1.5 percent silicon.

1920.

Aten, A. H. W. The electrochemical industry. 1920. Chem. Weekblad, **17**, 433, 441, 450, 461, 482, 493, 508.

Contains valuable bibliography.

Collins, E. F. Relative thermal economy of electric and fuel fired furnaces; cost tables. 1920. Gen. Elec. Rev., **23**, 768-73; C. A., **14**, 3597.

Data and cost of operation showing superiority of electric furnace. Electric furnace shows pronounced advantage, since it provides easy and positive temperature control and uniform heat distribution.

Contagne, Aimé. Energy consumption in manufacture of castings in electric furnaces (La consommation d'energie dans la fabrication des fontes au fours électrique.) 1920. Révue de Métallurgie, **17**, 450-68.

Comparison of theoretical and experimental data. Useful electrothermic effect on electric furnaces. Comparison of thermal efficiencies of electric furnace and blast furnace.

Dornbecker, C. Electric steel refined in the ladle. 1920. Schweiz. Chem. Ztg., 597.

Brief reference made to the duplexing process, in particular to the account of U. S. Pat. 1,318,164 given in Foundry 1919, **47**, 850.

Electric cast iron pipe. 1920. Iron Age, **106**, 1542; Chem. Abst. **15**, 804.

Mentions the desirability of lightweight cast iron pipe; use of electric furnace for treating cupola-melted iron. A

mixture sufficiently low in C and Si to result in a tenacious iron can be raised in the electric furnace to a sufficient temperature to make thin-section castings and at the same time clean the iron of impurities. The product shows a tensile strength of 30,000 to 40,000 lb. per sq. in., and a transverse strength (in the standard 2 x 1 inch bar) of 2600-3500 lb., with a deflection of 0.38-0.50 in.

Electric furnace developments in 1919. 1920. Blast Fur. and St. Pl., **8**, 45.

Notes on the increased application of electric duplexing, and the formation of Electric Furnace Association.

Electric furnace for experimental use. 1920. Elect. World, **57**, 265.

A hand-fed carbon-arc furnace has been utilized by the Pacific Foundry in the production of special cast irons, 2.8 percent carbon, from scrap otherwise unusable. The furnace is a two-phase Rennerfelt of 340 kg. capacity; experimental iron castings show a test of 40,730 to 45,030 lb. per sq. in.

Elliott, G. K. Electric furnaces and the sulphur problem in cast iron. 1920. Iron Age, **106**, 919; Foundry, **48**, 978.

Author refers to previous description of production of low-sulphur cast iron by a duplex process—refining a cupola-melted metal under a basic carbide slag in a basic bottom electric furnace. This produces iron containing less than 0.05 percent sulphur. The ability to desulphurize so thoroughly permits the use of cheap scrap high in accumulated sulphur.

Escard, Jean. Electrometallurgie du et de ses alliages. 1920. Paris, Dunod, 811 pp., 90 fr.

Comprehensive treatise on the electrometallurgy of iron, steel and alloys and electro-furnaces for their manufacture. Chapter 1, pp. 1-114, electric cast iron.

Keeney, R. M. The present status of the electric furnace in the American metal industries. 1920. Chem. and Met. Eng., **23**, 980-84; Chem. Abstr. **14**, 1936.

Gives a complete summary and review of the applications of the electric furnace. In particular, states that electric melting of scrap steel, etc., gives cheap pig iron. Transverse strength and sulphur content are improved by refining cupola iron in basic electric furnaces, especially for malleable castings.

Keller, C. A. Synthetic cast iron. 1920. Chem. and Met. Eng., **22**, 83-88, also Eng. and Ind. Manag., **2**, 515-20.

Outlines continuous process of rapid carburization during melting of steel turnings, said to produce cast-iron and semi-steel of exceptional purity and exact chemical analysis for manufacture of heavy shells and high grade castings. Novelty of manufacturing is said to consist of carburizing iron and steel scrap, and more particularly turnings, by melting these materials in presence of carbon, which is introduced simultaneously with them in melting appliance.

Moissan, H. Electric furnace. 1920. The Chemical Publish. Co., Easton, Pa., 313 pages.

Morrison, W. L. Manufacture of synthetic cast iron in the electric furnace. 1920. Elec. World, **75**, 1490.

Gives analyses and tests of several heats of grey cast iron made from wrought iron and steel scraps, in a 1000 lb. experimental electric furnace. The furnace was single-phase, operating with a conducting hearth and a single electrode above the bath.

West, Clarence J. Electric furnace as applied to metallurgy. 1920. Pub. A. D. Little, Inc., Cambridge, Mass., 92 pp. reprinted from Trans. Am. Electrochem. Soc., 1920, **38,** 365.

A bibliography from 1900 to 1919, inclusive, of the electris furnace applied to all the metal industries. Pages 31 to 49 deal specifically with the electric furnace and iron manufacture.

1921.

Brooke, F. W. Acid vs. basic electric furnace for the foundry. 1921. Chem. and Met. Eng., **24**, 794; also Foundry, **49**, 429-30.

Enumerates carefully the conditions determining the choice of acid or basic furnace in the foundry; when considering the refining of cast iron basic furnaces should be installed.

Cahill, W. E. Electric furnace practice at Treadwell. 1921. Min. and Sci. Press, **122**, 535; abstr. Iron Age, **107**, 1604.

Description of the 2-ton Heroult electric furnace at the Alaska Treadwell mine. With coke at $50 per ton, the cost of producing iron in the electric furnace is less than by melting in a cupola with coke. The iron is melted under a neutral or reducing atmosphere, and the metal is refined under a CaC_2 slag, which removes the sulphur. Perfect control of entire operation. Gives details of difficulties encountered and overcome.

Cawthon, J. L. Electric furnace grey iron. 1921. Elec. J., **18**, 396-400.

Discussion of costs and economy; comparison of cupola and electric furnace processes; consideration of temperature control, and quality of product.

Cope, F. T. Molten cast iron held without change in Baily electric furnace. 1921. Elec. World, **78**, 523.

Describes tests of duplexing method, melting the heavy scrap and pig iron in the cupola, discharging this molten metal into the electric resistance furnace, where it may be refined if necessary, and melting borings and turnings in holding furnace. The advantages are: the ability to maintain a uniform pouring temperature, the possibility of continuous pouring, and the fact that borings and turnings may be converted economically into good foundry iron.

Cost of melting cold metal in electric furnace. 1921. Elec. Rev., **78**, 890.

When cold scrap is fed into an electric furnace there are usually considerable current-voltage fluctuations until the scrap is melted. Data from steel melting show that 80 percent of total current consumed is used to melt the cold stock, the remaining 20 percent in the refining. Duplexing is not only cheaper, but it is also faster; but duplexing is dependent upon the running time of the cupola.

Elliott, G. K. Superheats in the electric furnace. 1921. Foundry, **49**, 714-9.

The cupola electric furnace duplexing process has been in successful operation in foundries for about 4 years, the largest passing over 200 tons of grey iron through the electric furnace every 24 hours. Describes conditions, temperatures, sulphur, phosphorus, manganese, carbon content, etc. In the U. S. duplexing costs $6 to $15 above the cost of ordinary cupola iron. Duplexing is eligible wherever high quality or strong insurance against defective castings is desired. It is not a foundry cure-all, but requires careful, intelligent supervision.

Gosrow, R. C. Cost of synthetic grey iron low. 1921. Foundry, **49**, 242, 311.

Synthetic iron made from steel scrap is cheaper than electric furnace metal made from iron scrap; gives cost analysis for making electrically melted grey iron from iron, also from steel.

Gosrow, R. C. Electric furnace possibilities in the western iron industry. 1921. J. Elec. **47**, 265-7.

An analysis of the opportunities open to the electric furnace in the western iron industry, with data on costs, accuracy of control and flexibility, which indicate its advantage in this field.

Hatt, H. L. Makes pig iron in novel electric furnace. 1921. Iron Tr. R., **68**, 149-51; Foundry, **49**, 30-2.

Description of a home-made electric furnace of simple construction operated to produce synthetic pig iron from steel scrap; could also be used to make grey iron or malleable iron.

Hay, Thomas Robson. Grey iron castings from electric furnace. 1921. Iron Age, **108**, 12, 14, 15.

Electric furnace replacing cupola first because of demand for superior iron, and second because of excessive cost and uncertainty of supply of ordinary foundry pig; electric iron is purer, carbon content can be better controlled, loss of alloys reduced and hotter metal poured.

Hodson, F. Electric melting of cast iron scrap. 1921. Iron Age, **108**, 283.

Discusses type of furnace needed to remelt scrap for production of grey iron. Only furnaces of arc type will give necessary temperature.

Melting cast iron scrap. 1921. Iron Age, **107**, 1686.

Results of tests satisfactory; cast iron borings and cast iron scrap were melted in a resistance type, non-ferrous Baily furnace; gives chemical analysis and power used.

Moldenke, Richard. Electric furnaces in the iron foundry. (Duplexing.) 1921. Iron Age, **107**, 437-9; also in Trans. A. I. M. E. No. 1044, 7 pages; same, Foundry, **49**, 216-18.

Discussion of duplexing process and of melting from cold metal. Advantages of each method. Use of basic hearth electric furnace yields metal with high degree of superheat, thoroughly deoxidized, and low in sulphur.

Moldenke, Richard. The electric furnace in the iron foundry. 1921. Trans. A. I. M. E. No. 1073, 73-77.

Discussion of Moldenke's previous paper by G. K. Elliott, W. N. Crafts, A. L. Stillman and H. A. Schwarts.

Pig iron held in molten condition in Baily furnace. 1921. Elec. Rev. **79**, 169.

Test conducted with a Baily furnace shows lack of variation in the composition of the pig iron remaining in the furnace in a molten condition for a period of 24 hours. Furnace 7 feet in diameter, capacity 1 ton. Borings heretofore not readily handled in any other type of furnace can be economically melted in this furnace; scrap metal can be melted repeatedly without the addition of fresh pig iron, since in the electric furnace there is no increase in sulphur as in the case with the cupola.

Schwarts, H. A. American malleable cast iron; electric furnace melting. 1921. Iron Tr. R., **68**, 1792-7.

Discussion of the triplex process, developed by W. G. Kranz, and involving use of cupola, converter and electric furnace; considers metallurgy and chemistry of the process, as well as heat balance sheets.

Stainless iron. 1921. Iron Age, **108**, Extract from Ironmonger, London.

A new low carbon chrome-iron alloy called "stainless iron." Carbon content 0.10 percent or less. Softer than stainless steel and hence more malleable. Said to be successfully used for auto parts subject to corrosion or tarnishing.

1922.

Barton, L. J. Synthetic cast iron, made in California. 1922. Chem. and Met. Eng., **26**, 270-71.

Successful trial runs made in a standard 6-ton Heroult furnace, making pig iron by melting steel scrap; cost $25 per ton against market price of pig iron in Sacramento of $45 per ton. Gives analysis of charge and of product and log of one furnace heat.

Morrison, W. L. Manufacture of synthetic cast iron in the electric furnace. 1922. Chem. and Met. Eng., **26**, 312.

Synthetic iron produced in electric furnace. Furnace linings and bottoms discussed and detrimental effects of excessively dry slags. Comparative costs of manufacture for various load factors.

Wilkinson, D. Electric furnace strengthens iron. 1922. Foundry, **50**, 143.

Brief review of work on synthetic pig iron production. Suggestion for inexpensive type of electric furnace for grey iron foundry.

DISCUSSION.

Bradley Stoughton[1]: On page 129 the authors mention an article by J. Escard and state that he "Reviews industrial processes of iron manufacture by means of electric furnaces." This should be electrolytic iron. It refers to the plant in Grenoble, France. The reference should be eliminated altogether from the paper.

[1] Consulting Engineer, New York City.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 28, 1922, President Acheson Smith in the Chair.

A PLEA FOR RATIONAL INTERPRETATION OF HYDROGEN ION MEASUREMENTS [1]

By William C. Moore [2]

Abstract.

It is pointed out that, in many biological systems, hydrogen ion regions are of more importance than actual hydrogen ion concentrations. Thus, invertase has a flat maximum of activity in the range for [H+] 1×10^{-4} to 1×10^{-5}, and, concurrently, fermenting molasses mashes show within this range no relation between hydrogen ion concentration and yield of ethanol. Finally, a plea is made to express hydrogen ion concentrations in any one set of measurements in terms of a common denominator instead of as "pH" values, which for chemical work sometimes seem inconvenient.

During recent years, much time has been given by scientists in many varied fields to a study of hydrogen ion concentrations in all sorts of physico-chemical systems. As a result, the literature on the subject has accumulated by leaps and bounds. Thus, in the decennial index of Chemical Abstracts, covering the period from 1907 to 1916 inclusive, the references to "Hydrogen Ion" cover about a page of space. In the index of the same journal for 1917, references to this subject cover about one-eighth of a page; for 1918, about one-sixth of a page; for 1919, about half a page, and for 1920, about three-fifths of a page. This latter index is particularly interesting, as indicating the breadth of the field—it ranges from mosaic disease of tobacco plants through that rare liquid, beer, to the thermodynamic properties of hydrogen ion in solutions of 0.1 M HCl containing uni-univalent salts.

In the writer's opinion, however, it seems desirable, at the present time, to call attention to certain considerations which are

[1] Manuscript received January 25, 1922.

[2] Research Laboratory, U. S. Industrial Alcohol Co., Baltimore, Md.

sometimes in danger of being overlooked in dealing with this important physico-chemical quantity.

In the first place, recognition of the facts that in an aqueous system it is generally possible easily to control the hydrogen ion concentration, and that variations in it are easily measured has undoubtedly led to the enormous amount of work which already has appeared.

In the second place, referring to the general equation for concentration cells,

$$E = \frac{RT}{nF} \log \frac{C_1}{C_2}$$

it is readily seen that since for any one ion, the valence, "n," is constant, the electromotive force E is a logarithmic function of the concentrations C_1, C_2. Conversely, we may regard in an actual hydrogen electrode measurement, the variable concentration C_2 (C_1 is to be taken as 1 normal), as a function of *E*. Now E is the intensity factor of electrical energy, E nF; and as such we must, therefore, always remember that hydrogen ion concentrations are a measure of the intensity factor in a hydrogen ion system, and as such must be sharply differentiated from total available acidity. From this standpoint it is easily seen that hydrogen ion concentrations alone may in some cases determine whether a reaction will proceed or not, and, if it proceeds, may determine the rate; but the total available acidity may have a decided influence on the ultimate condition of equilibrium. For this reason, the buffer content of an aqueous system may sometimes be of great importance.[3]

In the third place, even a cursory examination of the literature should convince one that in some cases the properties of aqueous systems are sharply dependent on hydrogen ion concentrations, while in others, the properties change materially only when the limits of certain hydrogen ion regions are exceeded. Within such regions it may happen that the hydrogen ion concentration is of relatively little importance. It is this latter statement to which it is proposed in this paper to give serious thought, since in

[3] J.V. Brown (J. Bact. 1921, 6 555,) has recently pointed out the importance of this point in titrating bacteriological media.

many biochemical fields, where an enormous amount of work has been done, we often meet with this "regional phenomenon," to which it seems only insufficient attention has been paid.

In leading up to this subject, let us first consider some typical aqueous systems where the properties are sharply dependent upon hydrogen ion concentrations. Perhaps the best example of this sort is found in the colored indicators. As is well known,[4] it is possible, by a suitable choice of these substances, to measure by relatively small increments, changes of hydrogen ion concentration over the whole range from 1×10^{-14} to 1×10^{-2}.

Coming to another phase of our topic, we find that among inorganic compounds we have an interesting class in the amphoteric hydroxides, which ionize to a greater degree as basic substances when the hydrogen ion concentration is greater than a certain definite value (characteristic for each such hydroxide) and which exhibit progressively increasing acid properties as the hydrogen ion concentration falls below this point. Using the equation,

$$(H^+) = \sqrt{K_w \left(\frac{K_a}{K_b}\right)}$$

developed by Michaelis[5] for this so-called "iso-electric point," it is easy where the dissociation constants, K_a as an acid and K_b as a base are known for any one hydroxide, to calculate the hydrogen ion concentration at which the change from predominant basic to predominant acid characteristics occur.

As an example we may use zinc hydroxide, whose basic dissociation constant, K_b is 145×10^{-11}[6] and whose acid constant K_a[7] is near 0.5×10^{-12}.

Using the value 1×10^{-14} for K_w, and modifying the equation to take account of the diacid and dibasic nature of zinc hydroxide, we find the iso-electric point for zinc hydroxide to be at a hydrogen ion concentration of the order of 1.3×10^{-8}. Here zinc hydroxide is least soluble; likewise least ionized; and probably shows inflection points in other properties.

[4] Clark, "The Determination of Hydrogen Ions" (1920).
[5] Nernst Festschrift, Halle, 1912, 308.
[6] Wood Chem. Soc. 97, 878.
[7] Slade, Z. anorg. Chem. 77, 457.

Inorganic hydroxides, however, are not the only substances exhibiting amphoteric properties. The amino-acids, as can readily be seen from a study of their structure, all possess this two-fold character. Recently, Eckweiler, Noyes and Falk have made a study of the iso-electric points of a number of these compounds.[8] Moreover, since the amino-acids are the units from which the poly-peptides and, in turn, the proteins themselves are built up, we should expect both these latter types of bodies to be amphoteric in their nature. The excellent work of Loeb[9] on the influence of hydrogen ion concentration on the properties of gelatine affords an example of the close relationship which may exist between degree of acidity and chemical behavior of such proteins.

In a somewhat different class falls the work of Beans, Fales and Ware[10] on the conditions under which zinc is precipitated quantitatively as sulfide. If the hydrogen ion concentration is above 1×10^{-2} the precipitation is by no means complete, while if it is below 1×10^{-3} the sulfide comes down in a slimy form difficult to filter.

Obviously, in the region 1×10^{-2} to 1×10^{-3} the conditions are at an optimum for the utilization of this method.

In an elaborate investigation on the mutarotation of glucose and fructose, Nelson and Beegle[11] have shown that there are certain hydrogen ion regions, the extent of which varies with the temperature, where the speed of this change is a minimum. Also, Nelson and Fales[12] show that the activity of invertase passes through a flat maximum at a hydrogen ion concentration of $1 \times 10^{-4.5}$. Above 1×10^{-5} the activity decreases rapidly; the same is true below 1×10^{-4}. Within the limits 1×10^{-4} to 1×10^{-5} relatively large change in hydrogen ion causes a relatively small change in activity.

In the above discussion, we have considered a few of the large number of relatively simple cases which have been investigated. In the examples quoted, it is plain that in some aqueous systems certain properties are dependent closely on hydrogen

[8] J. Gen. Physiol. 1921, **3**, 291.
[9] J. Gen. Physiol. 1919, **1**, 39, 237, 363, etc.
[10] J. Am. Chem. Soc. 1919, **41**, 487.
[11] J. Am. Chem. Soc. 1919, **41**, 559.
[12] J. Am. Chem. Soc. 1915, **37**, 2769.

ion concentration, while in other systems it is the hydrogen ion region which is important.

In most biological fluids, and in many manufacturing processes we have to deal, not with simple systems, but with very complex mixtures. It, therefore, is of great importance in working with such material to be sure that the range of hydrogen ion concentrations employed is sufficiently great, and that within each portion of the field other conditions be sufficiently studied to make sure that their influence is fully known. This is nicely illustrated by the work of Bunker[13] on the production of diphtheria toxin. Bunker claims that the attainment of a definite hydrogen ion concentration after a certain time interval is necessary for the production of the toxin; but Robinson and Meader[14] have proved that other factors, such as the proper conditions for pellicle formation and a proper food supply far outweigh the intensity of acidity.

Similarly, the writer has been able to show that in the fermentation of molasses to produce alcohol, the hydrogen ion concentration has nothing to do with yield of ethanol if care is taken that the actual acidity is between the limits 1×10^{-4} and 1×10^{-5}, which, as will be remembered, is the region of optimum invertase activity (Nelson and Fales, *loc. cit.*).

In this work of the writer's over 400 measurements were made, during all parts of the fermentation process, using the electrometric method. Some typical figures follow:

Hydrogen Ion Concentration in Fermenting Liquids.

All mashes contain 1 vol. H_2SO_4 to 2000 of mash.
Hydrogen ion concentrations x 10^5.

Run No.	221	222	223	224	225
Dona Yeast, set	1.82	2.19	2.14	2.09	1.91
Dona Yeast, end	2.63	3.09	2.69	3.17	2.09
Big Yeast, set	1.95	2.51	1.86	2.25	1.26
Big Yeast, end	2.51	2.19	1.66	2.51	1.78
Mash, set	2.79	....	2.09	5.01	1.15
Mash, 1 day	2.59	2.24	1.86	4.37	1.95
Mash, 2 days	....	2.04	1.86	4.47	2.19
Mash, 3 days	2.00	2.46	....	....	....
Beer	2.45	4.37	2.52	4.17	2.09
Alc. on total sugar....	93.37	93.73	88.88	93.88	93.27

[13] J. Bact. 1919, **4**, 379.
[14] J. Infect. Dis. 1920, **27**, 106-114.

In the table as given the figures shown are the average of at least two and generally several measurements. In every case, there had been regulation of the hydrogen ion concentration by the addition of sulphuric acid as shown.

However, molasses contains considerable buffer salts, and the addition of acid produces but little effect, as may be seen by noting the values as given below for molasses alone. Hydrogen ion concentrations of Porto Rican molasses, diluted with water, 1:4.5 = 0.98×10^{-5}. After adding H_2SO_4 1:2000, 4.67×10^{-5}. We must undoubtedly conclude that in fermenting molasses, the hydrogen ion concentration has little to do with alcohol yield, since the fermentation takes place within the region of maximum invertase activity. It is true, that if we go into a region of high acidity alcohol yields do depend on this factor; but this is to be expected when we remember that the activity of invertase decreases rapidly after the hydrogen ion concentration becomes greater than 1×10^{-4}.

If we want any further proof that hydrogen ion concentration may be of minor importance in a fermenting system, we have only to remember household practice in making preserves. Here the fruit is put up in a concentrated sugar syrup and never ferments, while if the same mixture were less concentrated fermentation would occur. Also, the concentrated molasses used in distillery practice may be kept for long periods without any great change taking place; it has to be diluted before being used. Yet the mere dilution of sugar produces no great hydrogen ion change, as these figures show:

Colorimetric Determinations of Hydrogen Ion Concentrations of Cane Sugar.

(Approximate values:)

1	Molar (phenol red indicator)	0.64×10^{-7}
1	" (Brom. thymol blue)	1.00×10^{-7}
0.5	" " " "	4.00×10^{-7}
0.2	" " " "	6.40×10^{-7}

Another consideration must be taken into account in studying biological systems. Almost all such, in their normal state, are heavily buffered—*i. e.,* contain such quantities of salts of weak acids or weak bases, generally in the form of organic amphoteric

substances, that the addition of a considerable quantity of an acid or of a base must be added before any considerable change in hydrogen ion concentration takes place. This, for example, is true of molasses, of blood, and of the nutrient media commonly used in bacteriological work.

When we consider these circumstances impartially, and in connection with such work as that quoted and reported above, it would seem that regions of hydrogen ion concentration are of more importance than the actual concentrations themselves. Thus, in Loeb's work, in regions above 2×10^{-5}, gelatine is a cation; in the region below this point it is anionic in nature. Similarly, in the region above 1×10^{-2} zinc is not precipitated quantitatively as sulphide; in regions above 1×10^{-3} invertase is inactive; it increases in activity in the region 1×10^{-3} to 1×10^{-4}; in the region 1×10^{-4} to 1×10^{-5} it has almost constant high activity with a flat maximum at $1 \times 10^{-4.5}$, and beyond 1×10^{-5} its activity decreases. Moreover, the type of curve exhibited by invertase activity is typical of biological systems in general, so that once the biologist has found the region of optimum activity for any particular system, he can forget about hydrogen ion concentration as an important variable as long as he is working in that region.

It will be noted that in this paper the use of the Sorensen index pH has been studiously avoided. It is the writer's belief that the disadvantages of this symbol outweigh its advantages. Briefly, the writer's reasons for the adoption of this viewpoint are as follows: If it is desired to plot concentrations over a wide field, it is granted that a logarithmic method is essential. It is also recognized that the transposition from potential measurements to pH values is simpler than going a step further and expressing such values as actual hydrogen ion concentrations. However, when one gets two values agreeing within two-tenths of a pH unit, the precision of such agreement leads to a false sense of accuracy. To give a specific example: pH values of 4.00 and 4.20 correspond respectively to actual hydrogen ion concentrations of 1×10^{-4} and 0.631×10^{-4}.

Likewise pH values of 3.4 and 3.6 refer to concentrations of 3.99×10^{-4} and 2.51×10^{-4} respectively. We thus see

that in different regions a difference of the same fraction of a pH unit leads to a much wider divergence of actual hydrogen ion values than at first sight would be apparent. Again, if we wish to compare actual magnitudes of sets of hydrogen ion measurements, Sorensen's system is inconvenient. To the writer, pH values are convenient in showing when several sets of results are of the same order of magnitude; and when once this order of magnitude is determined it seems better, more logical and more understandable to express the actual concentrations all in multiples of this "order of magnitude figure." Thus, in the work on molasses given above, the lowest figure is of the order of 1×10^{-5}, so all concentrations are expressed as multiples of this figure. The relation between the figures in this set of measurements is then easily seen by any one. Furthermore, by expressing results as multiples of some common number as is here done, the fact that more often than not regions of hydrogen ion concentration are of more importance than actual single values, is clearly brought out. Methods of expressing hydrogen ion concentration have recently been discussed by Wherry[15] and by Clark[16], so they will not be further elaborated here.

Summary.

(1) It is pointed out that in many systems, chiefly consisting of complex biological mixtures, actual hydrogen ion concentrations are of secondary importance so long as these values lie within certain definite hydrogen ion regions.

(2) It is shown that hydrogen ion concentrations are a function of the intensity factor of the energy.

(3) Figures are given for the hydrogen ion concentrations of fermenting molasses mashes.

(4) Within the limits 1×10^{-5} to 1×10^{-4} alcohol yield is not dependent on hydrogen ion concentrations.

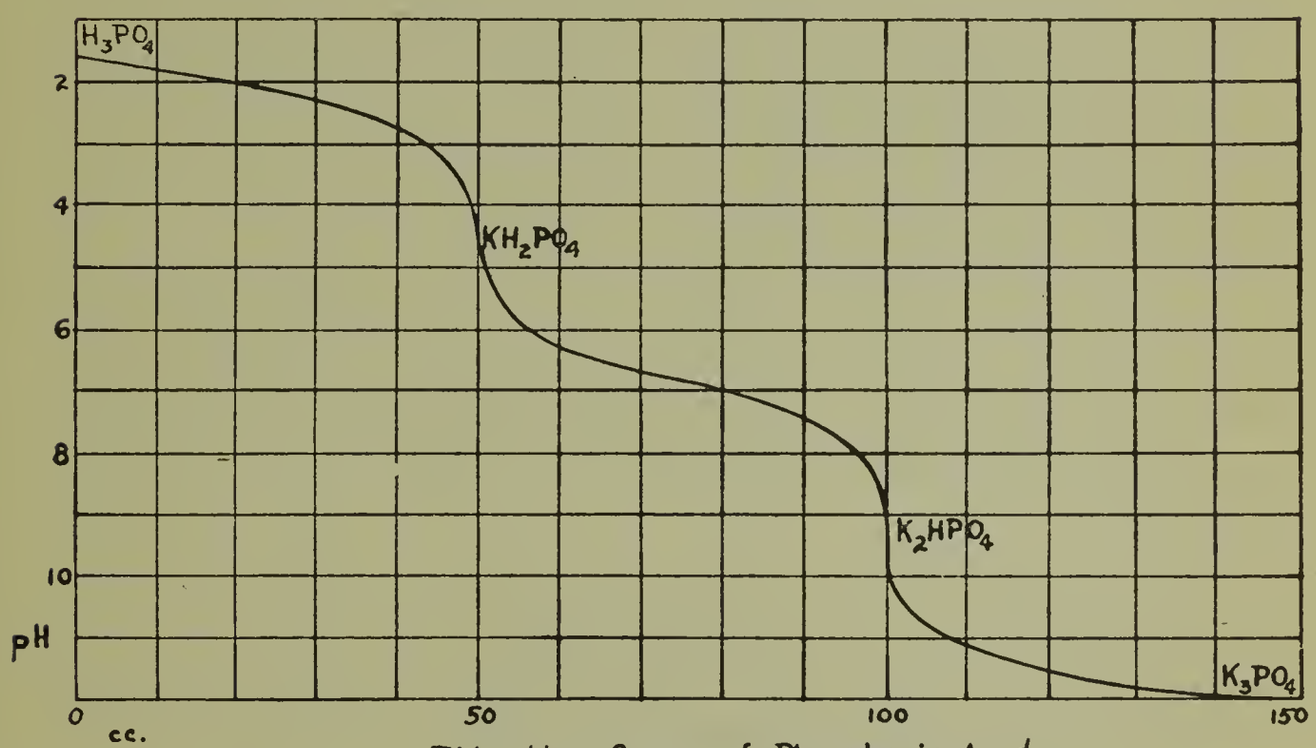
(5) A plea is made to regard pH values as indicating orders of magnitude only, since a clearer idea of conditions is given by

[15] J. Wash Acad. Sci. 1921, **11**, 197.
[16] J. Wash Acad. Sci. 1921, **11**, 199

expressing hydrogen ion concentrations in any one system in terms of some common denominator, which, of course, would vary with the system studied.

DISCUSSION.

CLARK E. DAVIS[1] (*Communicated*): Clark in "The Determination of Hydrogen Ions" p. 32 (1920) gives the titration curve of



Titration Curve of Phosphoric Acid.
50 cc. M/10 H_3PO_4 titrated with N/10 KOH.

Fig. 1

phosphoric acid (See Fig. 1). Examination shows that it requires exactly twice the amount of the alkali to gain the second end point as is used in the first.

This seems logical enough yet our actual titration values did not bear this out. Fig. 2 shows that the second end point is larger than the anticipated value of twice the first by an appreciable amount. This result is not accidental but has shown itself in repeated titrations and by different investigators.

Phosphoric acid was made by allowing pure P_2O_5 to stand in

[1] Research Laboratory of the National Biscuit Co., New York City.

contact with conductivity water for 48 hours, then refluxing for 1.5 hours. This solution was standardized against M/5 NaOH using methyl orange as indicator.

Sodium hydroxide was pure and entirely free from carbonate and made up with conductivity water and preserved in paraffined lined bottles. This same NaOH was used in titration of various other acids with results entirely regular.

The first break in the curve is undoubtedly the correct one showing the neutralization of the first hydrogen ion.

The second break being larger than the first is probably including some effect of the third hydrogen ion which is adding itself to that of the second. Just why this should be we are not certain.

Record must also be made that when the acid was added to the alkali the same relationship existed between the end points. However, these curves were not mirror images of each other due to different quantities of salts formed.

In a communication from Clark he says, "The middle portion of the curve Fig. 1 was not followed throughout its length in the actual experiment since a few experimental points showed that for the purpose under consideration it was sufficient to transfer the data."

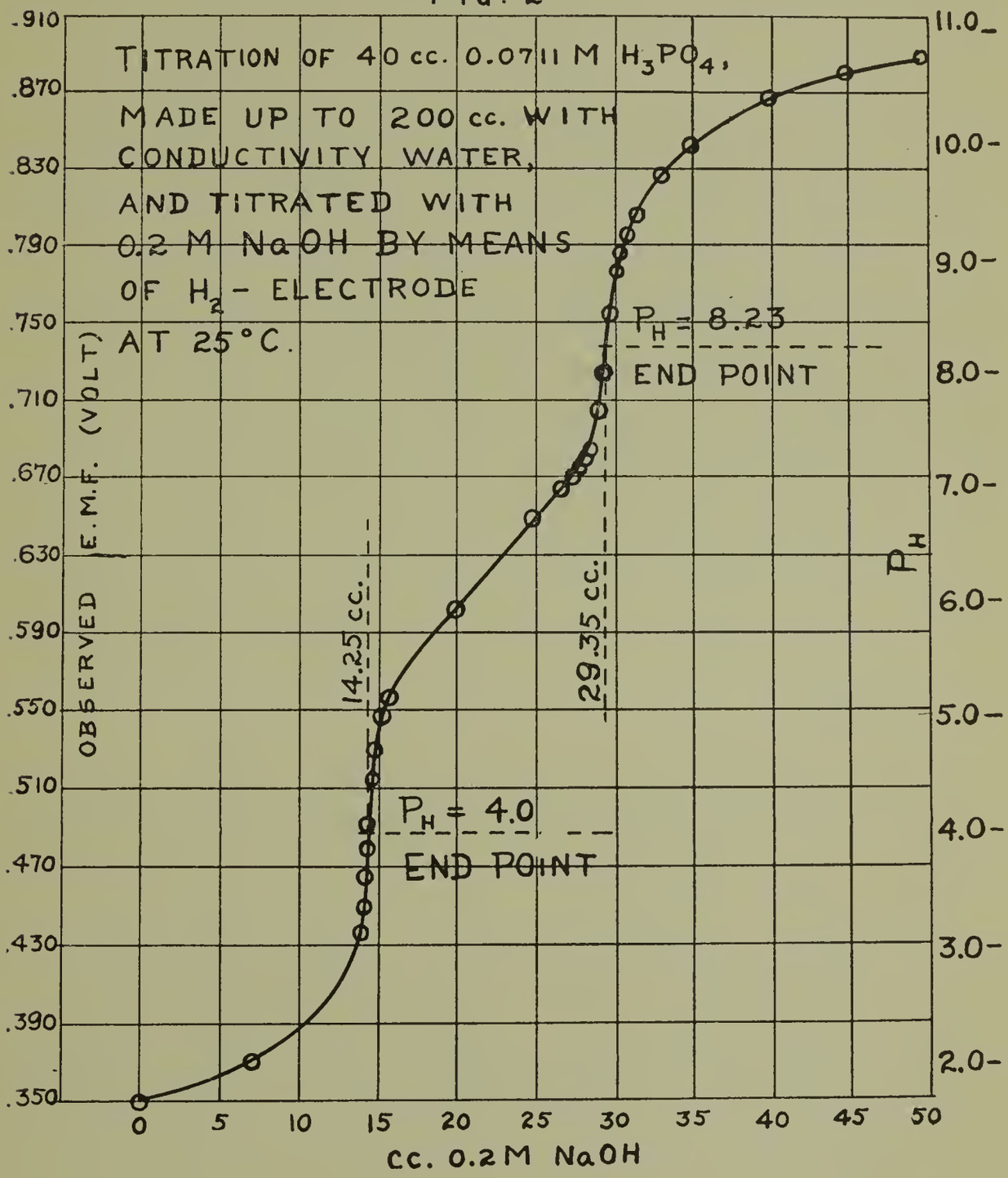
I wish to register myself as very much in favor of the Sorensen method of expression in certain circumstances.

Hydrogen-ion-concentration has been absorbed to a very large extent by the industries. Here it is of major importance to have a symbol of expression such as pH in preference to a more complicated form using a minus power of 10. Should you be called upon to talk with factory operators or with production men about acidity, the simplest way it can be done is in units from one to fourteen or more. It becomes a comparatively easy task to explain in a short time what is meant by pH and it is not long before the average uneducated worker in the plant will be speaking pH and using pH.

I question the advisability of changing the procedure and trying to tell him the same thing in units of $1 \times 10^{-7.5}$ for example. It seems to me that both methods of expression have their merits and it should be left to the judgment of the experimenter to make his choice.

Mr. Bowman of the United Chemical and Organic Products Company in a private communication says: "I make the point that the uncertainties involved in the interpretation of conductivity

FIG. 2



data, and of concepts like "Fugacity" and "Activity" have led to such a definition of pH that it is no longer to be taken as exactly equivalent to log $1/H_+$. (*Cf.* Clark, Det. of H-ions, p. 203, "The standard experimental meaning of pH shall be the corrected difference of potential between . . . ," etc.)

The symbol pH thus has a unique place as the standard experimental homologue, so to speak, of log $1/H_+$. It is a sufficiently close approximation to the latter for most practical purposes without being involved in its theoretical subtleties. The way should, therefore, be left open for the use of either symbol according to need.

W. C. Moore: As I mentioned at the beginning, Dr. Keyes first called this work of Dr. Davis to my attention and told me he had discussed this very fully with Dr. Davis and that he had an explanation to offer; namely, that when we are using a hydrogen electrode for titrating acids with bases, we must be sure to take into account the fact that the water with which our solutions are made is an active part of the system. We ordinarily do not do that. In the neutralization of an acid and a base, if we formulate the reaction in accordance with the law of mass action, we regard the water as constant. It is Dr. Keyes' idea that the activity of the water is not constant and should therefore be included and it is because of that fact that this discrepancy with what we first think is the right result and what is the experimental result, really arises. If there are any questions about this paper, I shall be glad to answer them.

Wm. Blum[2]: There is one point in the paper with regard to the question of the relative utility; it is purely a matter of convenience; we are all talking about the same values. In this paper the author states, discussing the values on page 144, "we see in different regions, a difference of the same fraction of the pH unit leads to a much greater divergence of hydrogen ion values than at first sight would be apparent." I would simply call attention to the great convenience of the logarithmic system involved, that is, as a similar increment always represents the same relative change in the hydrogen ion concentration, it does not matter whether we have a change from pH 2 to 2.3, or pH 5 to 5.3 it means that we are reducing the hydrogen ion concentration to one-half. In each case, and since this is an intensity factor rather than quantity, we are much more concerned with the rate at which it is changing than the actual magnitudes. We think that hydrogen ion concen-

[2] Chemist, Bureau of Standards, Washington, D. C.

tration is very closely analogous to temperature measurement. We do not care whether our temperature measurements represent actual calories or not; all we care about is that we have a certain scale which is definite and reproducible; so from that standpoint I believe that the pH system is simpler and can meet all the requirements which can be met by the exponential system.

C. P. MADSEN[3]: Dr. Moore's conclusion that the reactions he investigated are the function of a range or region of hydrogen ion concentration rather than of a definite figure, applies also to other reactions. I have found that it applies to the electrodeposition of metals from strong electrolytes, particularly nickel. I also agree with Dr. Moore in his preference for Sorensen's pH nomenclature for general use. In the case of strong electrolytes, however, other factors than that of hydrogen ion concentration may influence the millivolt readings, and in these cases I prefer to record the results in terms of millivolt readings only. If any other nomenclature is used in these cases, that of the pH is preferable because it follows the millivolt reading linearly.

[3] Consulting Engr., New York City.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 28, 1922, President Acheson Smith in the Chair.

EXPERIMENTS WITH ALTERNATING CURRENT IN DIRECT CURRENT ELECTROLYSIS.[1]

By W. B. Jones.[2]

I. INTRODUCTION.

Electrochemical literature shows that by superimposing an alternating current on direct current in electrolysis, a decrease in electrode potential is obtained. This is manifested by measurements of overvoltage, and by the character of the products from electrolysis, more of the intermediate products and less of the end products being obtained. Since the exact cause of overvoltage is not well understood, and since methods of properly measuring it are in some respects doubtful, it is obvious that it would be difficult to make similar measurements with combined alternating and direct currents. Some literature has reported negative overvoltages under such circumstances, which at once opens the question as to the suitability of the method employed.

The word "overvoltage" is understood to be the excess potential required to discharge an ion at the electrode above the potential of a reversible electrode in equilibrium with the same ion. Accordingly, overvoltage exists only while current flows, so that to obtain correct values current should be flowing when measurements are made. Such a measurement always involves a potential caused by resistance of the solution, resistance of the electrode and any resistance which may exist between the solution and the electrode by virtue of the liberation of gas. These extraneous potentials have been eliminated by extrapolation, or by momentarily breaking the circuit and measuring the back e. m. f. as the overvoltage. These methods have not been applied in using a superimposed alternating current on direct current.

Data on potentials reported in the literature dealing with alter-

[1] Manuscript received February 29, 1922.

[2] Buffalo, N. Y.

nating current and direct current electrolysis give the effective potential, which is a function of current flowing. In the work reported below almost instantaneous values of current and "measured potential" are found. An apparently true correction has been applied for ohmic drop measured, leaving what is assumed to be the true overvoltage. The most outstanding feature is that variations during the cycle are followed, rather than the effective value over a complete cycle. Owing to the nature of the method and difficulties involved, mathematical precision has been sacrificed.

II. PURPOSE.

The purpose of this investigation was:

1. To study the cathodic overvoltage of lead electrodes in sulphuric acid during direct current electrolysis by superimposing alternating current in an amount sufficient to give:

   a. No reverse current
   b. Reverse current without corrosion.
   c. Reverse current with corrosion
   d. Reverse current to equal cathodic current.
   e. Reverse current greater than cathodic current

2. To study cathodic overvoltage using an intermittent direct current.

III. RESULTS.

1. The overvoltage of lead as cathode is found to be about 1.1 volts with direct current alone.

2. This overvoltage is a maximum and exists only while current flows.

3. On stopping the current, the back e. m. f. exerted by the electrode falls from the value of its overvoltage at about 1.1 volts to 0.5 volt in 0.08 second, at which time it is falling at the rate of five volts per second.

4. If in place of stopping the cathodic current a reverse current is used, the overvoltage drops more rapidly to a constant level at about 0.18 volt.

5. As the reverse current is continued a point will be reached beyond which the lead becomes anode, corroding to lead sulphate before forming a protective oxide film.

6. If reverse current is not continued until the corrosion takes place, but is replaced by cathodic current, the overvoltage will rise almost linearly with the quantity of electricity passing, reaching a maximum when sufficient coulombs have passed to equal or exceed that amount which passed as reverse current.

7. When the maximum overvoltage is reached, the number of hydrogen atoms deposited on a fresh lead surface is about three times the number of lead atoms exposed at the surface of the electrode.

8. It is concluded that cathodic overvoltage of lead is caused by the formation of higher hydrides which are increasingly unstable.

9. In the case of anodic overvoltage of lead reverse current produces a change of only 0.05 volt, because of the greater stability of the oxide film.

10. As soon as a molecular film of oxide or hydride is formed, overvoltage has been established.

IV. METHOD.

1. *Electrical Arrangement.* In general the method used in this work was to take the direct current and alternating current circuits mutually independent, and to apply the effect to either the cathode or to the anode and not simultaneously to both.

Figure 1-A represents a simple cell with anode and cathode. B represents the same with two cathodes in parallel connected outside the cell. C shows the secondary of a transformer in series with the two cathodes, the middle of the secondary being common terminal for the cathodes and the D. C. source. Such a connection causes the direct current to buck itself in the transformer, provided equal currents flow in the cathode circuits. This keeps the D. C. and A. C. circuits mutually independent. It should be borne in mind that the alternating current flows only between the two cathodes of the D. C. circuit.

Figure 2 shows the working arrangement with resistances for current control and adjustment. Non-inductive resistances were used. Alternating and direct current ammeters were calibrated. It is to be observed that the reading of an alternating current

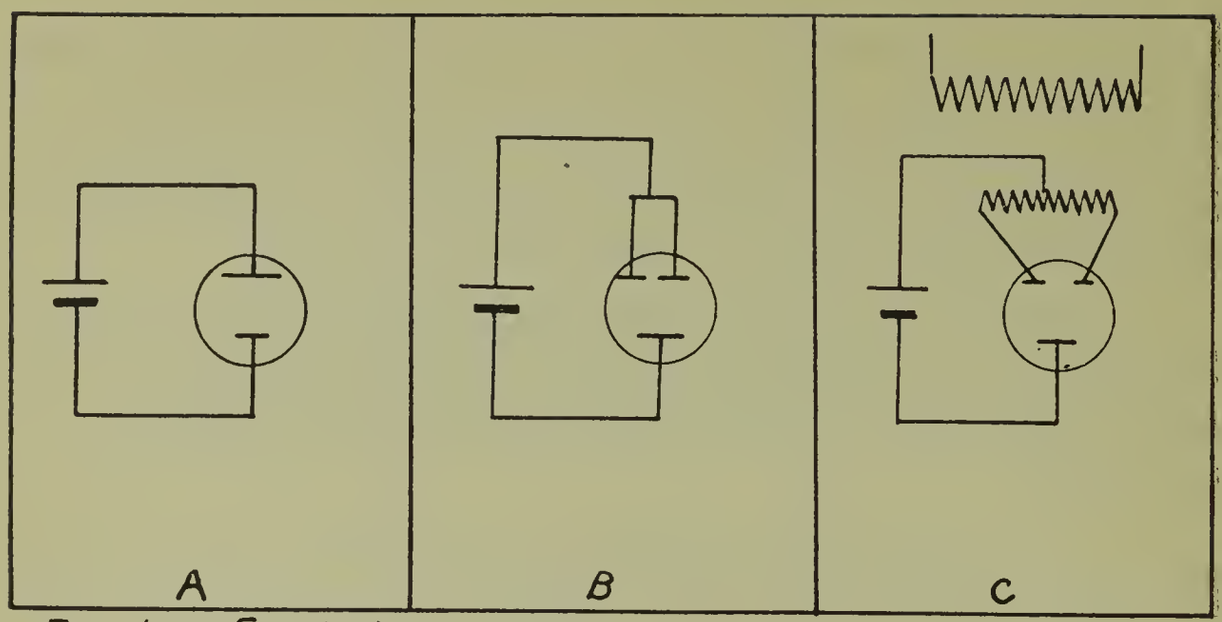


Fig. 1. Evolution of the cell.

1. Transformer Primary 110 A.C.
2. " Secondary
3. V.R. To Regulate A.C.
4. Storage Battery
5. V.R. To Regulate D.C.
6. V.R. To Equalize D.C.
7. D.C. Ammeters
8. A.C. Ammeter
9. D.C. Ammeter
10. Equivalent Cathodes
11. Common Anode
12. Shunts for Current Meas.

Fig. 2. Details of cell

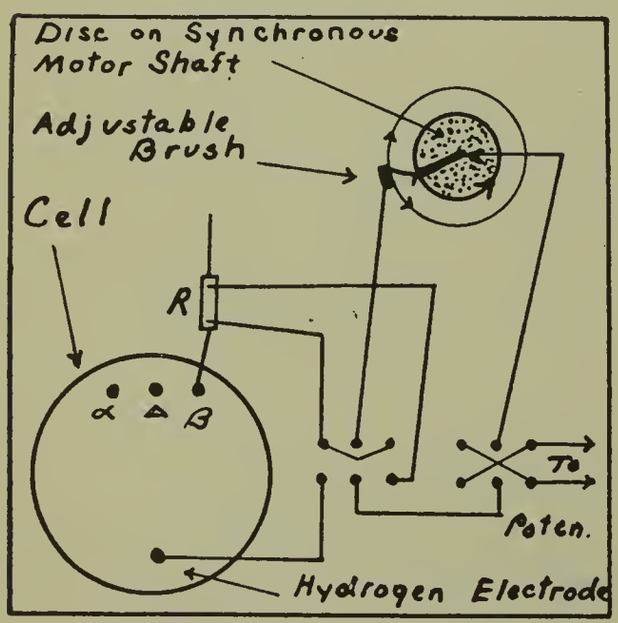
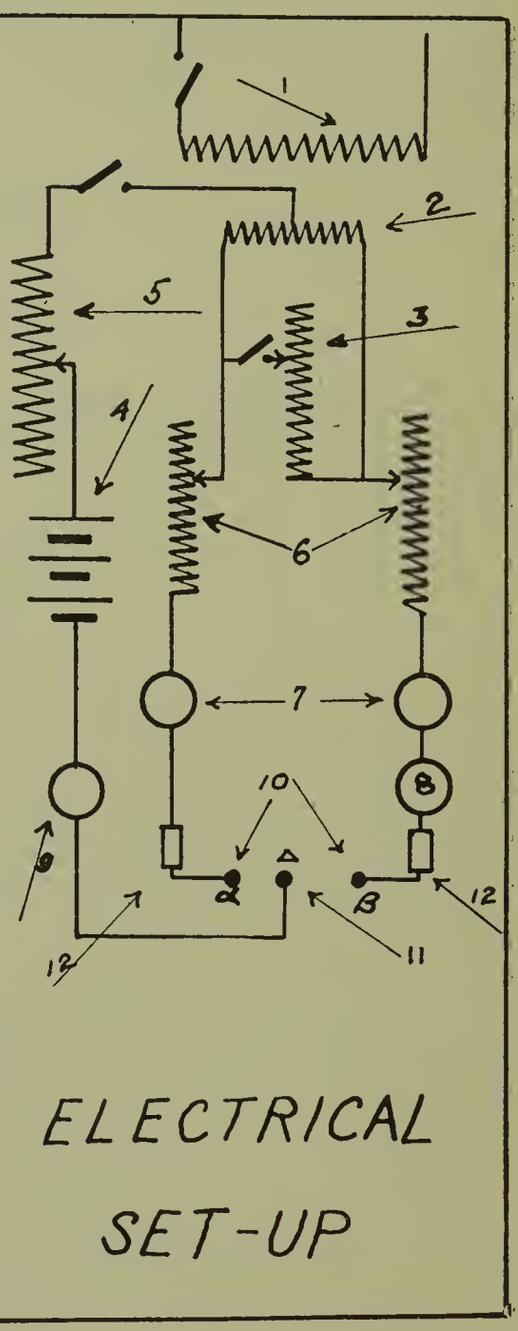


Fig. 3. Contact Device



ammeter is the square root of the sum of the squares of the direct current and the effective alternating current amperes.

Figure 3 shows the arrangement of the cell with potentiometer connections. A 10-inch crystallizing dish with the three electrodes and the reference electrode is used. Of the three electrodes delta is at all times anode (or cathode), while alpha and beta are similar cathodes (or anodes) at which the alternating current is superimposed. A large volume of electrolyte compared to the electrode has been chosen to minimize changes in concentration by electrolysis of added ingredients or by corrosion of the electrodes themselves. A symmetrical arrangement is maintained so that the alpha and beta electrodes are duplicates with respect to the delta electrode and to the reference electrode.

It should be particularly emphasized that the electrode under study, say beta, is at all times a cathode to the delta electrode and alternately anode and cathode to the alpha electrode. When the anodic action to the alpha is so great as to overcome the cathodic action to the delta, the beta electrode will in itself function as an anode, but is considered still as a cathode with reversed current.

2. *Potentiometer System.* This consists of a Leeds & Northrup Potentiometer, Type K, box type portable galvanometer, and Type R d'Arsonval galvanometer. As the range of the potentiometer is 0 to 1.6 or 0 to 16 by construction, modifications were made so that the range became 0 to 4.8. This makes the scale divisions more convenient for rapid adjustment, and covers the ranges found in the experimental work. The effect is to change the factors from 1 and 0.1 to 3 and 1.

3. *Contact Device.* When the alternating current is superimposed upon the direct current the result at a single electrode is a varying current of sine wave form, with its axis displaced to a position corresponding to the value of the direct current. Consequently when the maximum value of the alternating current is greater than the direct current a reverse current flows through the electrode. If an almost instantaneous contact to a sensitive potentiometer system can be made at the same point in repeating cycles, a method of study can be developed comparable with direct current experiments. This has been done in such a way that any point in the cycle can be taken.

A motor operated synchronously by the same source of alternating current has a fiber disc upon its shaft, Fig. 3. This disc contains an inlaid metal segment corresponding to an arc of 10 degrees. A brush consisting of two spring copper wires makes contact with this segment for 10 degrees during a cycle of 0.04 second or for 0.00111 second. The brush is adjustable about the axis of the motor by divisions of its circumference into 360 degrees. This gives an arrangement whereby single measurements can be taken varying in time by 0.000111 second, each measurement being the average value for 10 degrees in a cycle.

Two double-pole double-throw switches are also shown in Figure 3, one to serve as a reversing switch to the potentiometer terminals, and the other to connect the potentiometer to the beta electrode and the reference electrode for potential measurements or to the calibrated resistance R for current measurement.

4. *Reference Electrode.* A normal calomel half-cell is available at all times for use. It has been found that under the method employed where contact to the electrode is made for only 0.00111 second the impulse is weak because of the high resistance of the calomel electrode. Consequently a hydrogen electrode is used for such measurements, since this is immersed directy in the cell. However, the calomel electrode has been used in some instances in the experiments following. For the hydrogen electrode, hydrogen was obtained from a pressure tank, washed through alkaline permanganate, water, passed over heated copper, through a soda lime tube, water and then to the cell.

5. *Sign of Potential.* The measured potential and overvoltage are given positive values in reference to the hydrogen electrode, the latter being the positive terminal. When a negative value is shown the hydrogen electrode is the negative terminal. The overvoltage of a lead anode is expressed as that of a cathode with reversed current, and consequently is considered a negative cathodic overvoltage.

6. *Experimentation.* In making each run, the cell is set in operation as desired and current adjustments made until equilibrium is established. This varies according to conditions, and is determined by observation of the ammeters and by repeating measurements at the same point in the cycle. It is necessary to

keep equal currents flowing in both alpha and beta circuits. The synchronous motor is also allowed to run to reach an equilibrium condition, since the heating or changing friction causes a lag of armature position with respect to that position it would occupy were it frictionless and of no resistance. Changes in line voltage are factors beyond the control of the operator, and contribute to unavoidable errors which have not as yet proven serious.

When equilibrium has been established measurements are taken by adjusting the brush position on the contact device, and by changing the electrical connections to the cell or shunt in the electrode circuit. About one hour is required to measure a single cycle of current or potential. Instances where a marked break occurs for any reason are discarded.

V. DATA FROM EXPERIMENTAL WORK.

1. *Explanation.* The measured data consist of potential in volts measured:

a. Across 1 ohm resistance in electrode circuit
b. Between lead electrode and reference electrode

for various positions of the brush on contact device. These data are shown on graphs with amperes and volts plotted against position in the cycle. These graphs are marked "data." From each data chart are tabulated simultaneous values of current and potential. These are plotted on a second graph marked "current-potential." Upon these graphs graphical corrections are made to eliminate ohmic drop, and the corrected curve is shown in dotted lines marked overvoltage.

In the data chart are plotted amperes against position in the cycle which is time. Consequently the area below the ampere curve is coulombs. From the current-potential chart are tabulated simultaneous values of current and overvoltage. A third value corresponding to current and position in the cycle as found in the data chart is the area proportional to coulombs which have passed up to that point in the cycle. This area is estimated or measured by the planimeter and calculated to scale and factor giving approximate coulombs. Simultaneous values of coulombs and overvoltage are plotted and marked "coulombs-overvoltage."

In order to eliminate many bulky tables curves only are shown in this paper. As an example, however, complete tables for experiment No. 2 are given as this is the first typical case.

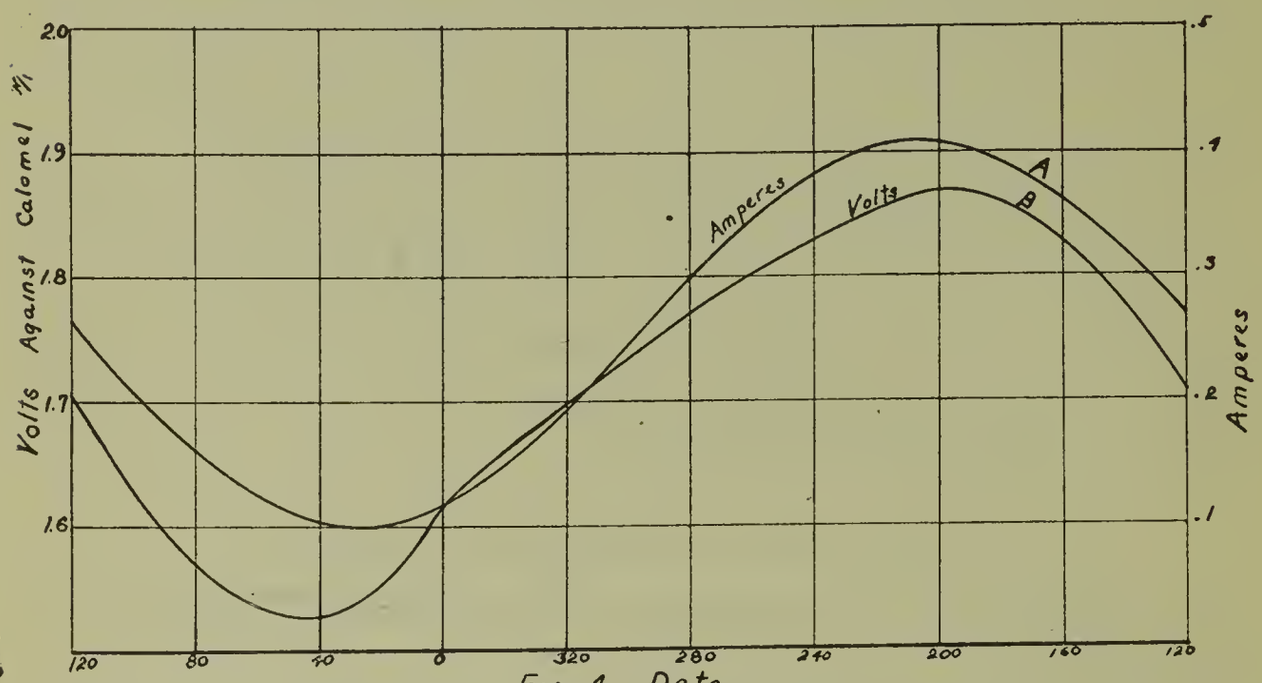


Fig. 4 Data.

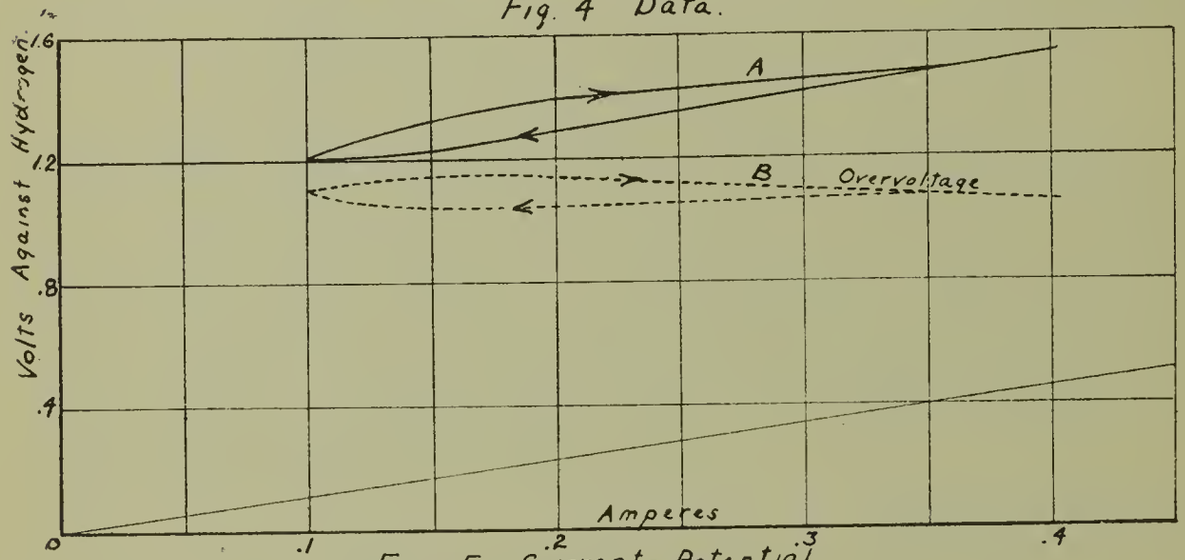


Fig. 5 Current-Potential.

EXP. No. 1

Experiment No. 1.

Purpose. To superimpose alternating current upon direct current so that no reverse current is obtained.

Electrodes. Lead cathode 1/16 x 1/8 x 1 inch immersed, (1.6 x 3.2 x 25.4 mm.).

Solution. Normal sulphuric acid.

Temperature. Not regulated. Room temperature, about 25°C.

Direct Current. 0.250 amperes. Area 0.375 sq. in. (2.42 sq.

cm). Direct current density 0.666 amp. per sq. in. (0.103 amp. per sq. cm).

Alternating Current. Effective value 0.1 ampere.

Data. See Fig. 4.

Discussion. Examination of Fig. 4 shows only changing potential with changing current. Converting values against the calomel electrode to the hydrogen electrode, and plotting simultaneous values of current and potential, a new relationship is found.[3]

Fig. 5 represents the current-potential relationship. Curve A is the measured potential against current. It shows a decided slope. The assumption is made that this is due to ohmic resistance. Justification for this assumption is more apparent from later experiments. The slope of the line from tip to tip of the enclosed area is taken as the ohmic resistance. A parallel line through the origin furnishes the ordinate to be deducted from the observed potentials.

Curve B represents curve A corrected for ohmic drop. The bulging of the curve at the left is not explained. The average of the two curves is taken as the overvoltage at 1.11 volts using a direct current density of 0.666 amp. per sq. in. (0.103 amp. per sq. cm.) cathode in $N/1$ sulphuric acid with an alternating current of 0.267 amp. (effective) per sq. in. (0.041 amp. per sq. cm.)

Experiment No. 2.

Purpose. To superimpose alternating current upon direct current so that a slight reverse current is obtained.

Conditions. Same as Experiment No. 1.

Data. This experiment, recorded in Table I, is a typical example of the table used to produce the three types of charts for each experiment. Fig. 6 was plotted from the results of this experiment. Examination of the curve B in Fig. 6 shows that the potential does not fall below zero when the current is reversed as might be expected. No general relationship is evident from these curves. By construction of the current-potential chart, more evidence is found as recorded in Table II.

[3] The hydrogen electrode used in later experiments was found to be negative to the calomel by 0.323 volt.

Fig. 7, showing the current potential was plotted from Table II. Curve A shows itself to be practically linear beyond 0.15 ampere. The portion against decreasing current is linear practically at all

TABLE I.

Position of Brush in Cycle	Milliamperes Thru Electrode	Position of Brush in Cycle	Millivolts Against Hydrogen Electrode
73	0.00	0	265
3	0	10	130
10	—13	20	120
30	—40	30	134
40	—47	40	210
50	—47	50	376
60	—38	60	546
70	—14	70	740
90	+78	80	885
120	256	90	979
140	380	100	1086
160	483	110	1167
180	550	120	1257
190	569	130	1330
200	578	140	1410
210	577	150	1468
220	572	160	1515
230	553	170	1551
240	522	180	1582
260	443	190	1599
290	271	200	1610
310	161	210	1610
330	102	220	1610
350	45	230	1605
		240	1604
		250	1545
		260	1513
		270	1444
		280	1409
		290	1322
		300	1268
		310	1180
		320	1098
		330	832
		340	493
		350	250
		360	177
		360	211
		360	160

values of cathodic current. The conclusion is drawn that a constant overvoltage has been attained at 0.15 ampere ascending, which remains constant until current reaches zero. Consequently

the linear portion of the line represents ohmic drop in voltage which is observed with the overvoltage. Drawing a line through the origin, parallel to the straight part of the curve, gives ordinates which can be deducted from the observed potential.

Curve B is the corrected form of Curve A and represents the overvoltage. This shows that the overvoltage increases from a low value to a constant value until current is reversed, when it falls to the original low value. The form of the overvoltage curve does not show all the relations since there is no time factor

TABLE II.

Values of Potential from Fig. 6, Curve B.	Values of Current from Fig. 6, Curve A.	Values of Potential from Fig. 6, Curve B.	Values of Current from Fig. 6, Curve A.
0.15	0.0	1.58	0.550
0.17	0.01	1.51	0.487
0.25	0.035	1.40	0.380
0.47	0.065	1.26	0.260
0.70	0.085	1.08	0.140
0.86	0.100	0.87	0.025
1.00	0.117	0.80	0.000
1.08	0.130	0.75	—0.012
1.17	0.170	0.57	—0.035
1.25	0.215	0.38	—0.047
1.39	0.325	0.29	—0.050
1.51	0.440	0.19	—0.047
1.59	0.520	0.14	—0.044
1.62	0.570	0.12	—0.033
1.62	0.580	0.13	—0.015

involved in the graph. However, from this curve B and from Fig. 6, curve A, coulombs and overvoltage may be related, as shown in Table III.

The coulombs-overvoltage curve (Fig. 8), was plotted from Table III. This curve shows that the overvoltage is constant at 1.02 volts during the major portion of cycle, dropping slightly as current density decreases towards zero, just before reversal. During the flow of reversed current it drops to 0.15 volt, where it appears to remain constant for a short time until current is again reversed and made cathodic. After this point is passed it rises rapidly in a straight line, and then gradually approaches the upper limit of 1.02 volts. It is noticeable that the coulombs of

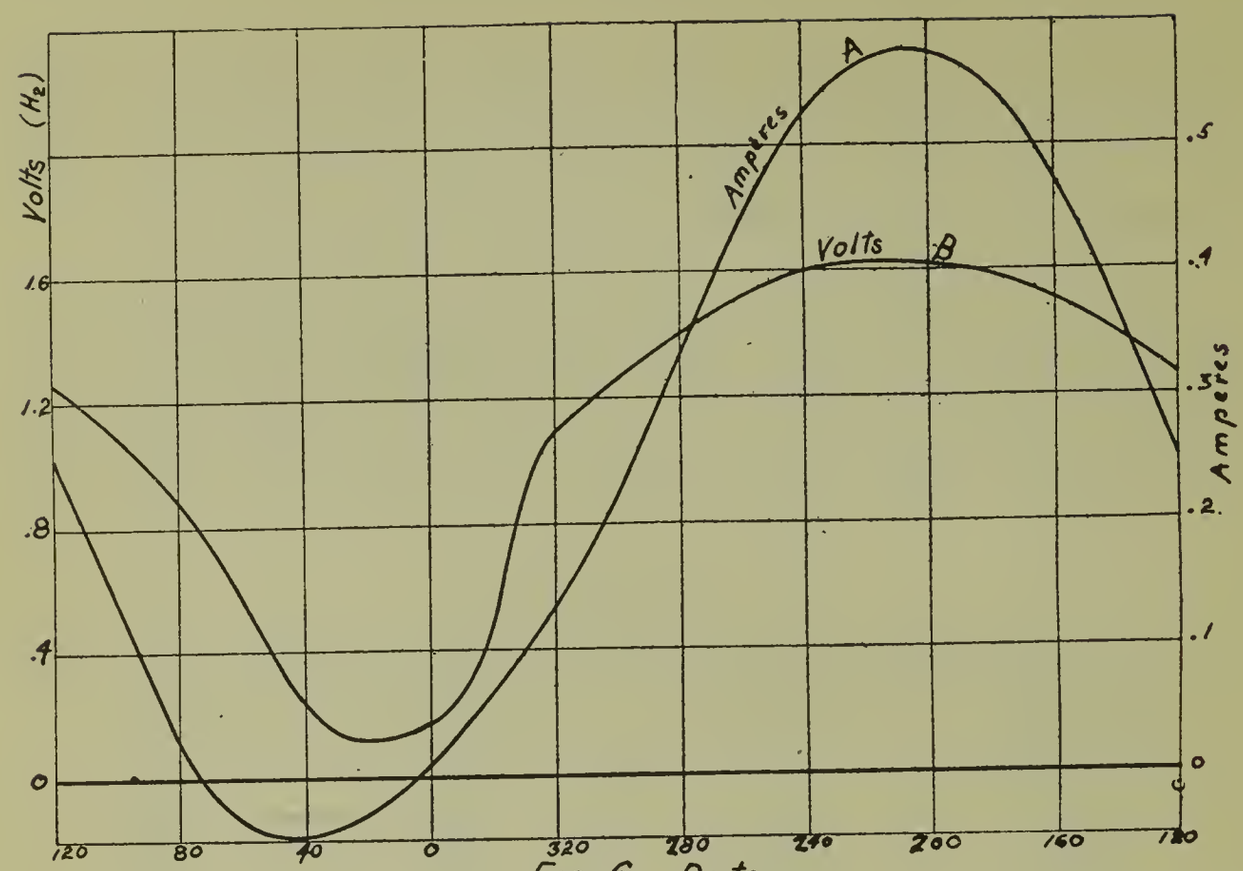


Fig. 6 Data

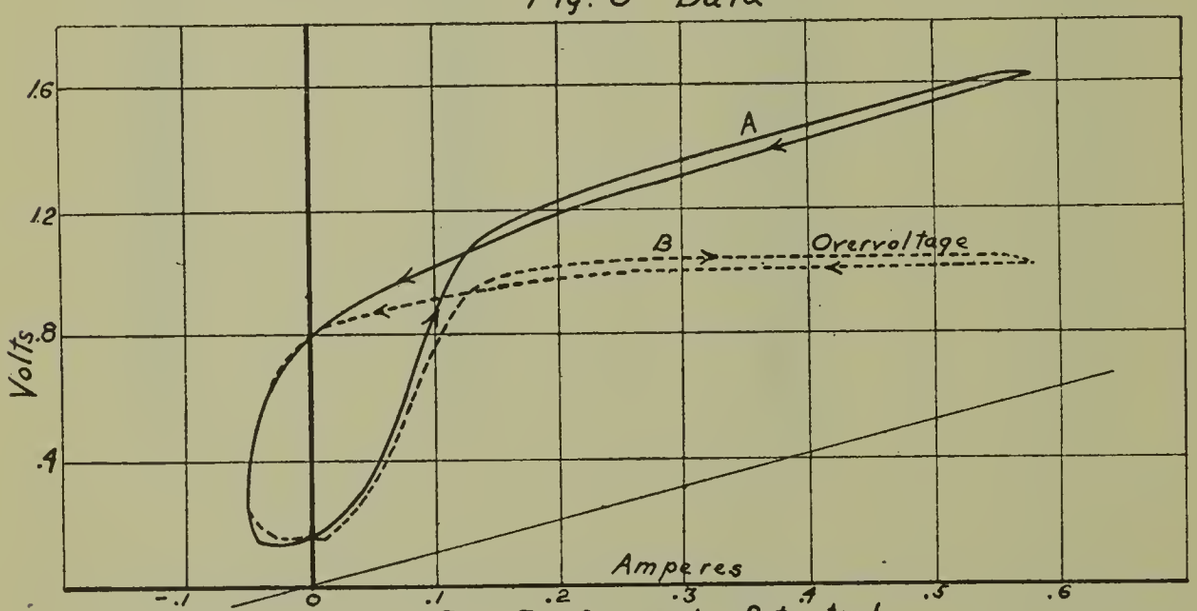


Fig. 7. Current- Potential.

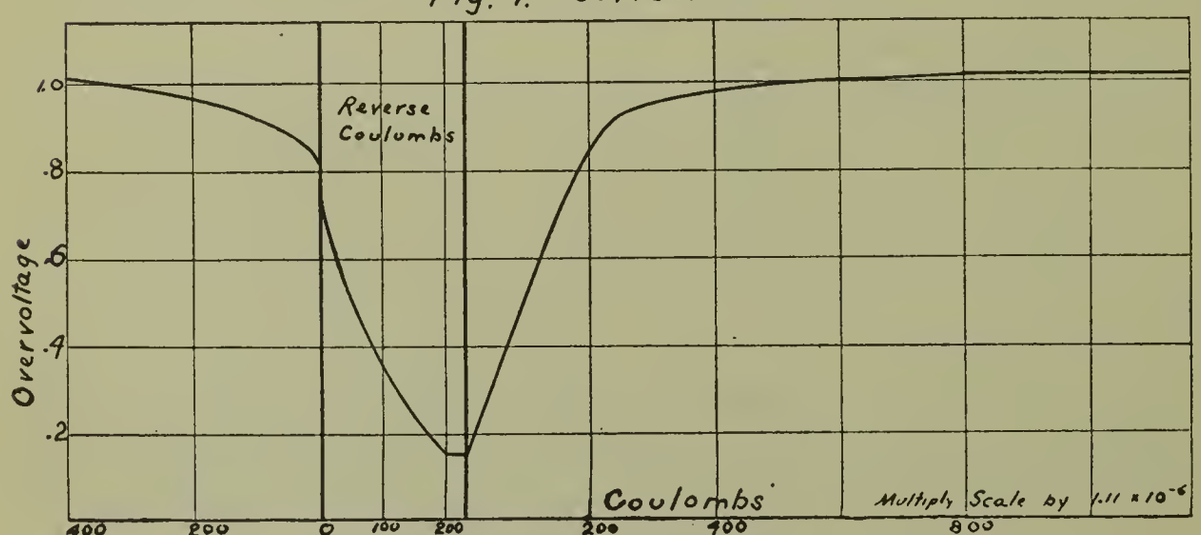


Fig. 8. Coulombs- Overvoltage

EXP. No. 2.

cathodic current required to build it up to the knee of the curve is approximately the same as the coulombs of reverse current which flow, namely 230 on the abscissa scale. This indicates a storage of hydrogen in some form on the cathode, which causes

TABLE III.

Overvoltage from Fig. 7, Curve B.	Amperes from Fig. 7, Curve B.	Area, Proportional to Coulombs, from Fig. 6, Curve A.*	Notes
1.02	....	....	Operating as cathode previous to reversal.
1.01	0.2	370	
0.96	0.15	210	
0.92	0.10	100	
0.87	0.05	27.5	
0.84	0.025	7.5	
0.80	0.0	0.0	Point of reversal
0.74	0.015	4.5	Reversed current flowing
0.65	0.03	21.1	
0.53	0.04	40	
0.30	0.05	126	
0.18	0.04	182	
0.15	0.025	216	
0.15	0.000	231	
0.20	0.025	13	Building up as cathode
0.30	0.050	47.5	
0.52	0.075	170	
0.76	0.100	101	
0.93	0.125	260	
0.97	0.150	350	
1.00	0.200	560	
1.02	0.250	800	

* One unit = 0.005 ampere
One unit = 0.000222 second
Therefore one unit area = 1.11×10^{-6} coulombs.

overvoltage. As this hydrogen is removed the overvoltage is lessened, and rises again only when the same amount of hydrogen has been put back into storage.

Experiment No. 3.

Purpose. To superimpose alternating current upon direct current so that a considerable reverse current is obtained without corrosion of the electrode.

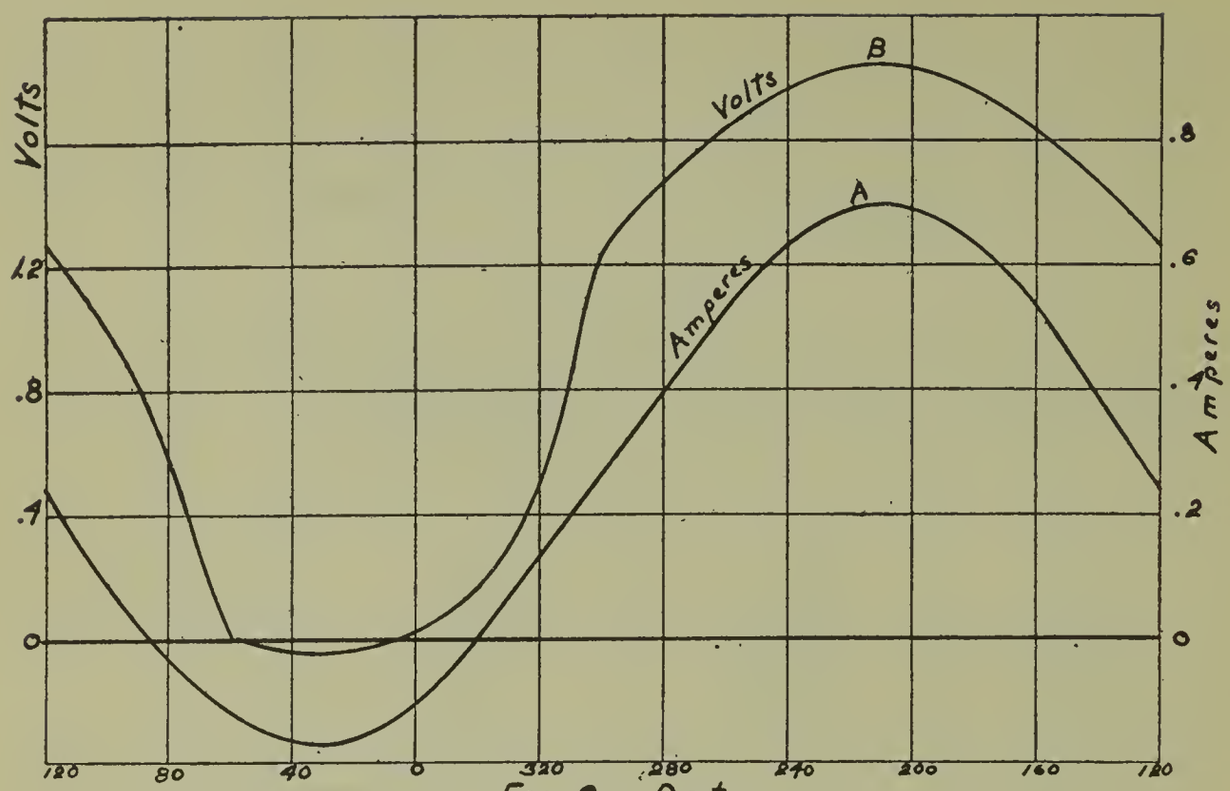


Fig. 9. Data

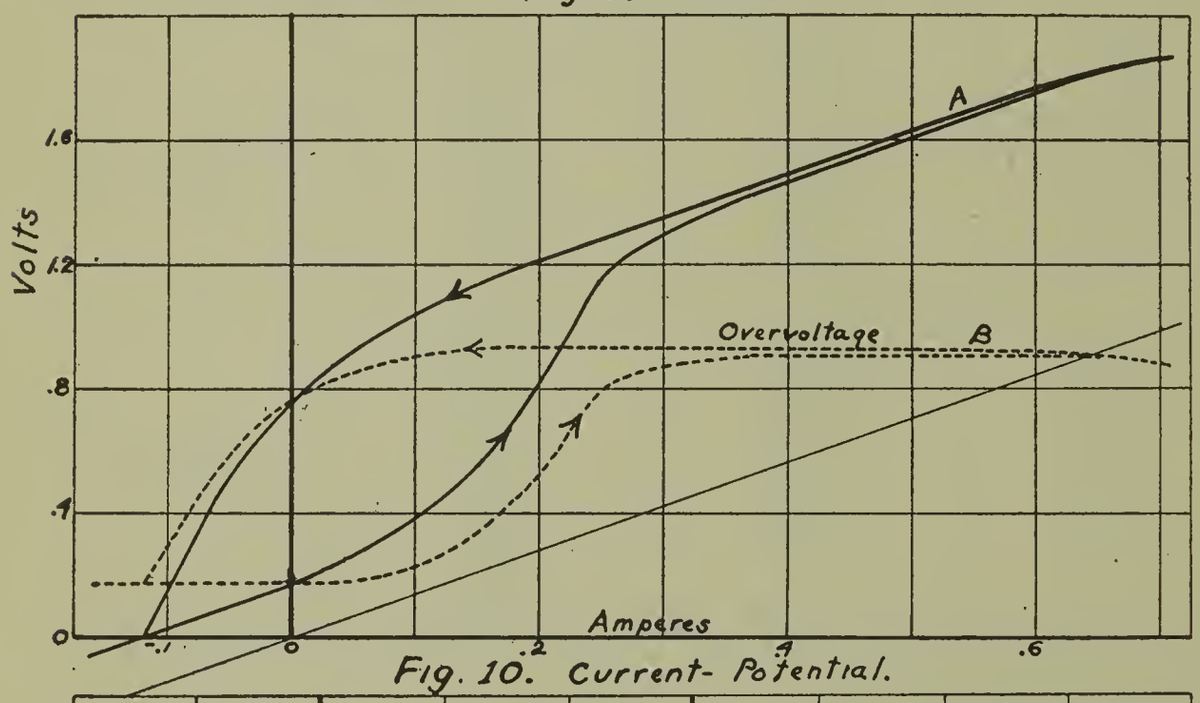


Fig. 10. Current- Potential.

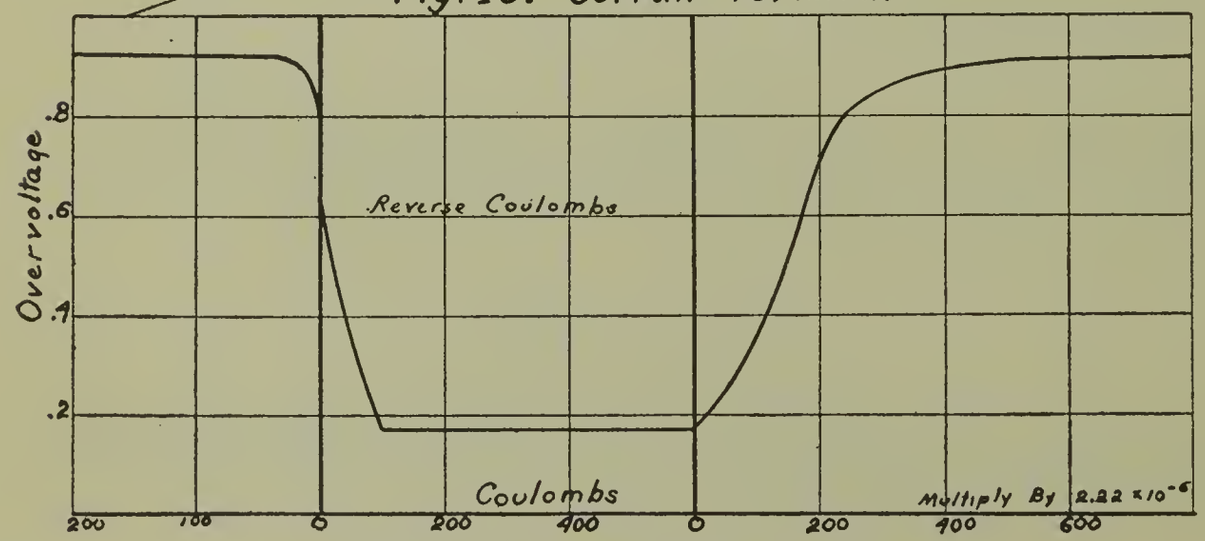


Fig. 11 Coulombs-Overvoltage.

EXP. No. 3.

Conditions. Same as Experiment No. 1.

Data. Shown in Fig. 9. Curve B shows a measured potential below the value of the hydrogen electrode. The significance of this is apparent from the next figure.

Current-Potential. Figure 10. This is plotted by the same procedure used in the last experiment.

Curve A shows again the linear relationship between potential and current, both as cathode and as anode where the reverse current approaches zero. The two lines are parallel, and this indicates that the resistance which causes ohmic drop is unchanged for these portions of the curve, and therefore is most probably constant throughout the cycle. This further justifies the procedure adopted for making corrections for ohmic drop.

Curve B is the corrected form of curve A and represents the overvoltage during the cycle. The full significance of the curve is better represented by the next figure.

Coulombs-Overvoltage. Figure 11. This shows the variation in overvoltage caused by the reversal of the current. As in experiment No. 2, 2.22×10^{-4} coulombs are sufficient to depolarize the electrode to a constant value of about 0.16 volt. In the former case reversed current ceased (see Fig. 8) when this value had been attained, but in this case (Fig. 11) reversed current is continued beyond this point and no change in overvoltage occurs. One would believe that if the storage of hydrogen were used up by the reverse current, it would take place at the value of the hydrogen electrode, or zero overvoltage.

Two theories are offered as explanation.

(A). A chemical compound of hydrogen and the lead is formed, which has a characteristic potential of about —0.16 against the hydrogen electrode.

(B). The storage of hydrogen at the electrode is decreased by the reversed current, and removal takes place at the potential of the hydrogen electrode. However, because of the reversed current the solution is depleted of hydrogen ions and approaches neutrality. The difference in potential thus caused would be manifested as overvoltage. The latter theory, however, does not

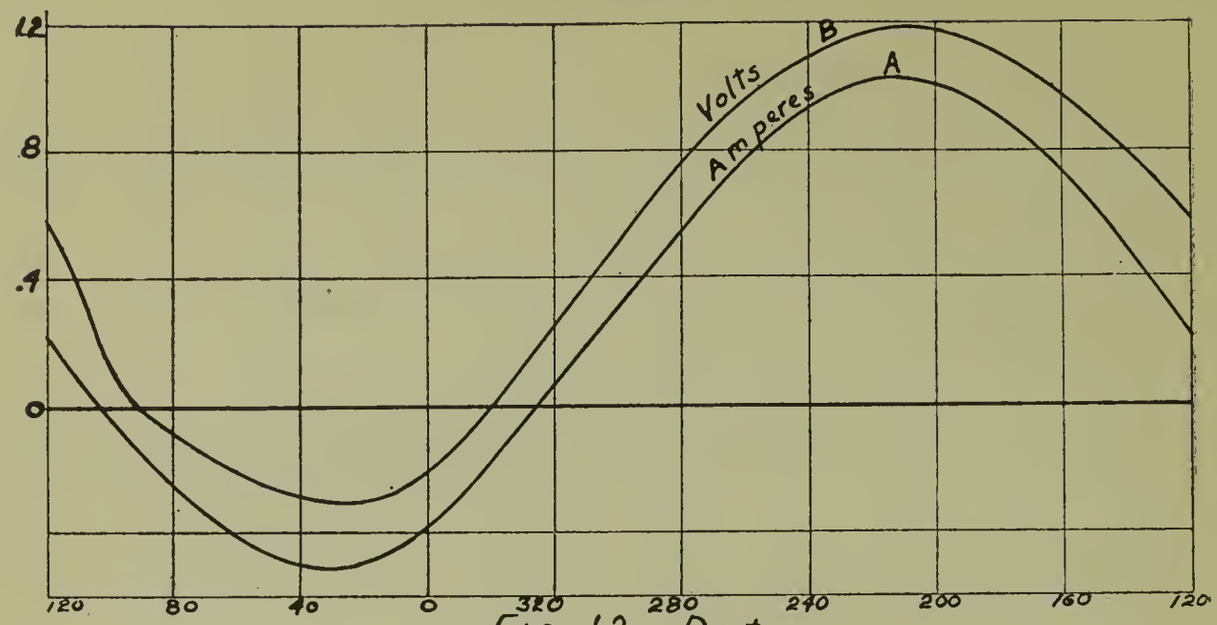


Fig. 12. Data.

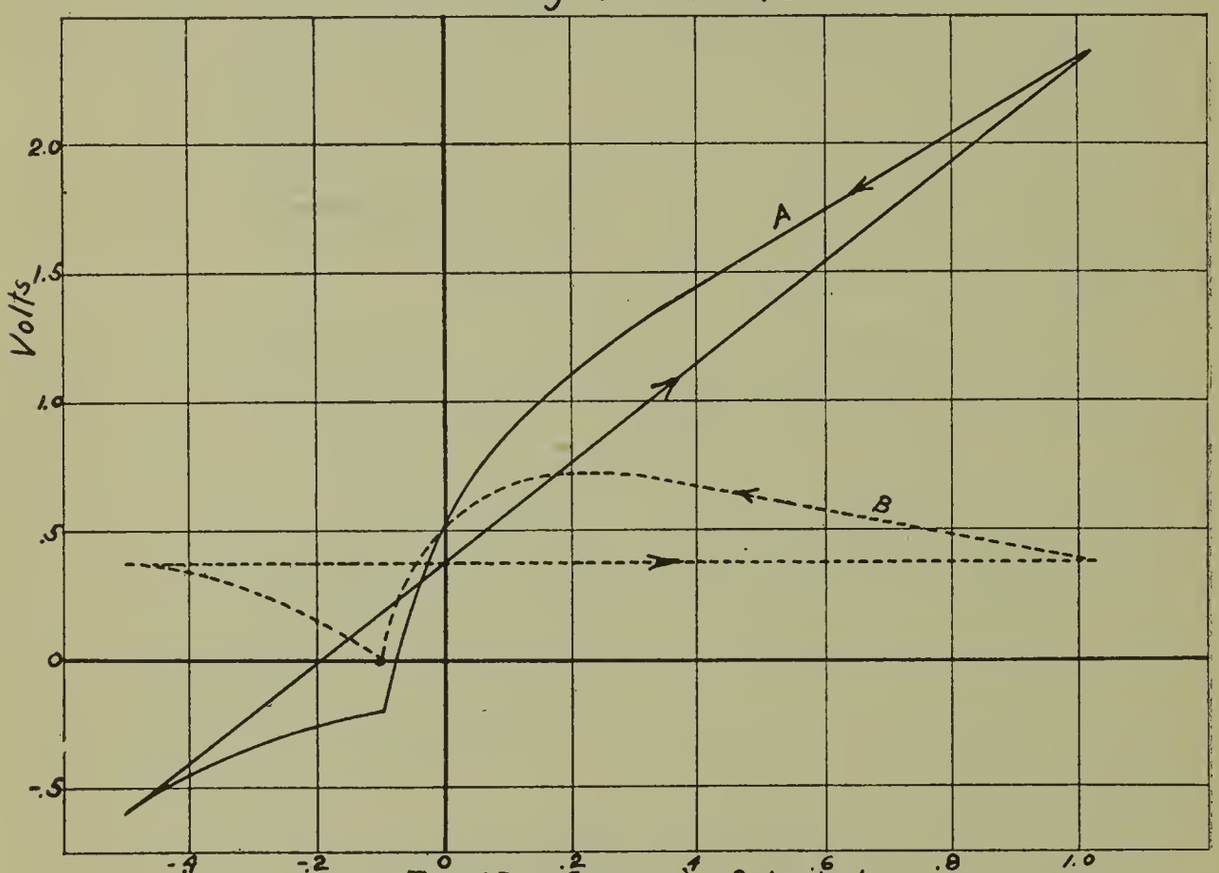


Fig. 13. Current - Potential.

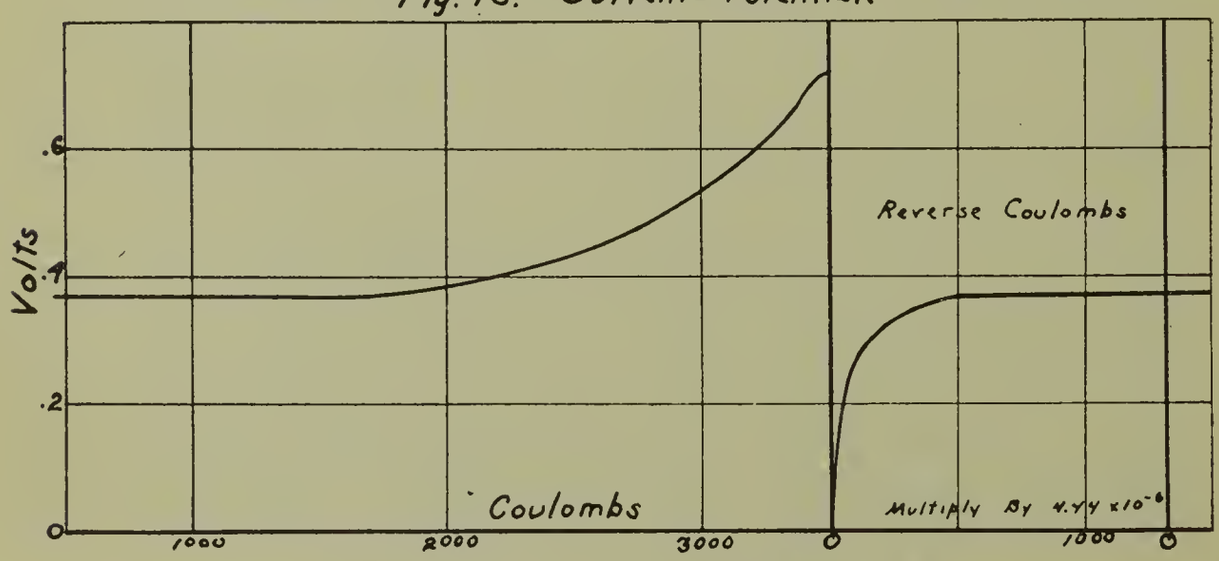


Fig. 14. Coulombs - Overvoltage.

EXP. No. 4.

account for the constancy of the potential. This confirms the former theory in preference to the latter.

In discussion of Figure 8 it was noted that the coulombs of cathodic current required to restore the overvoltage were equal to the coulombs of reverse current flowing. In Figure 11, this ratio is about 2 to 1.

Experiment No. 4.

Purpose. To superimpose alternating current upon direct current so that the reversed current causes corrosion.

Conditions. Same as Experiment No. 1.

Data. Figure 12.

Current-Potential. Figure 13. Plotted by usual procedure. Curve A shows the potential to be a linear function of current, from the maximum reversed through zero to the maximum cathodic current. The slope of this line is taken. Curve B is curve A corrected for ohmic drop by the procedure adopted.

Coulombs-Overvoltage. Figure 14. The results of this experiment as represented by this curve are not apparently in accord with the remaining experiments here described. This curve shows that by reversal of current the cathodic overvoltage is destroyed and falls exactly to zero. Further reverse current renews the overvoltage up to a constant value of 0.38 volt which remains unchanged with changing direction of the current. Further hypothesis on this experiment is omitted until more evidence is obtained.

Experiment No. 5.

Purpose. To make the reverse current equal to the cathodic current, or in other words, to use alternating current alone.

Conditions. Same as Experiment No. 1. The use of alternating current alone removes the delta electrode which has been functioning as anode. This makes the cell a simple one with two electrodes with alternating current.

Data. Figure 15. Curve C is a duplicate of Curve B, but is 180 degrees behind it as would be expected. The limit of the potentiometer at the time this experiment was performed was

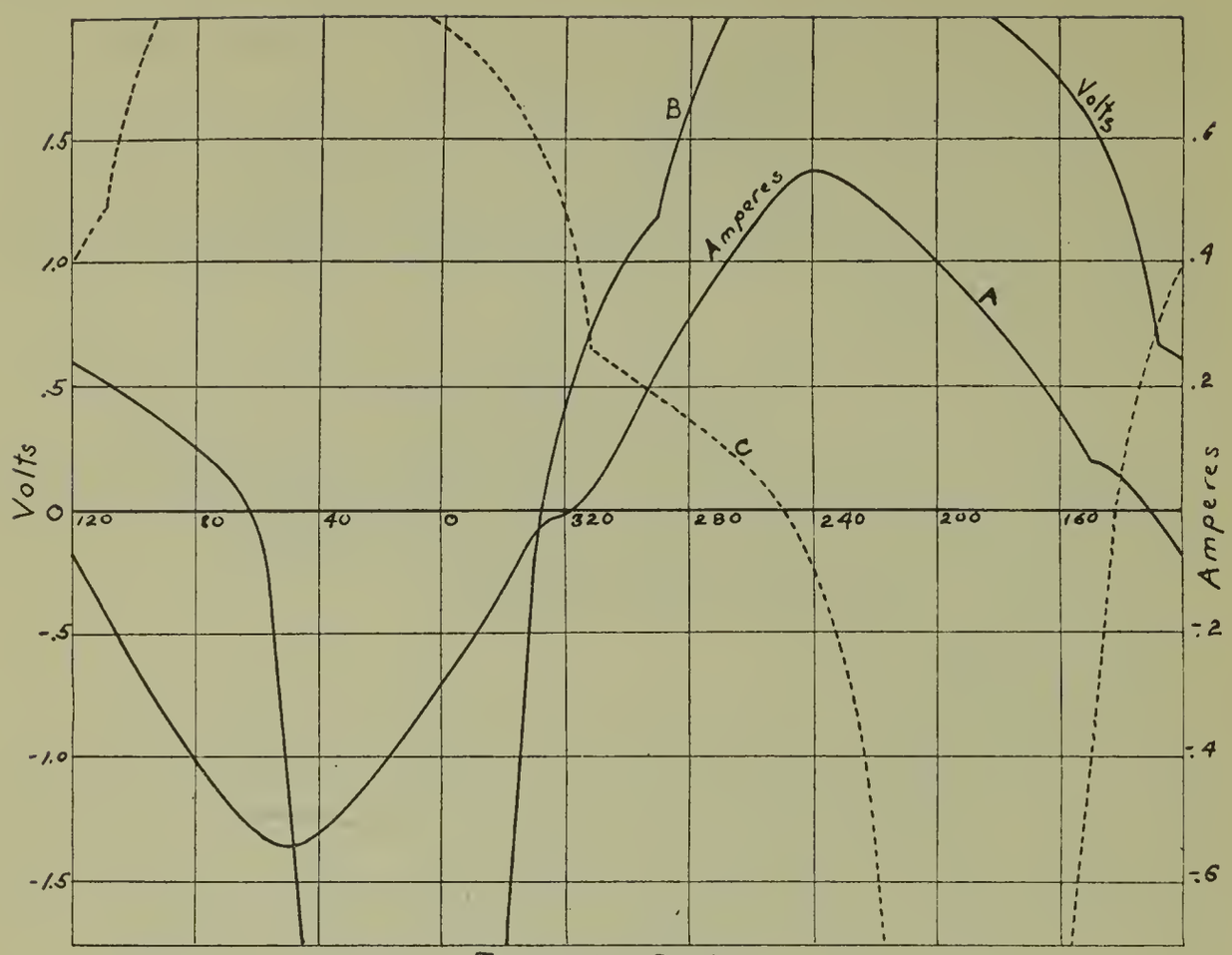


Fig. 15. Data.

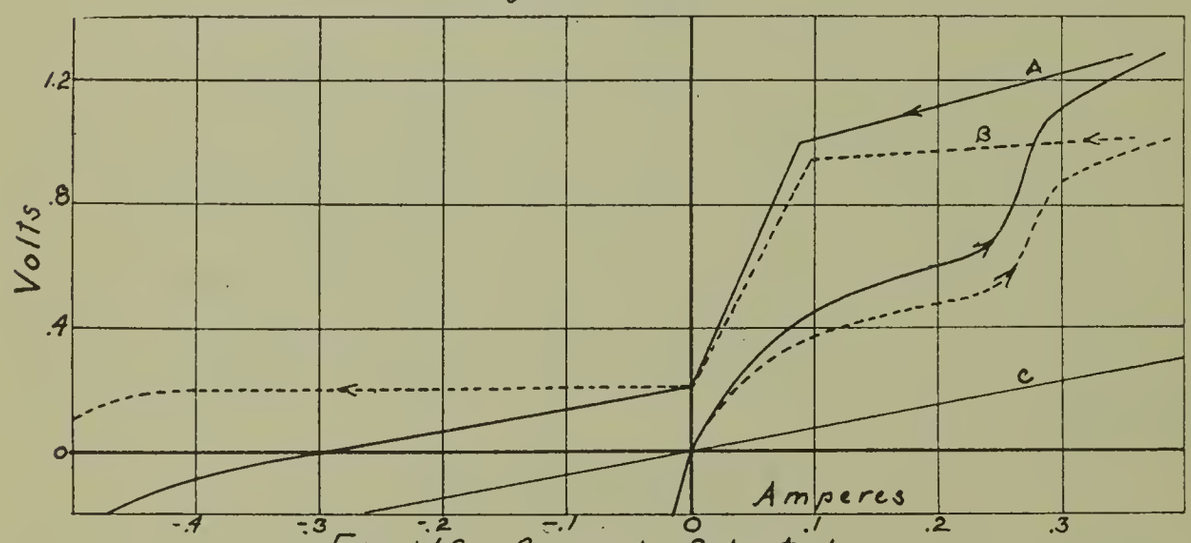


Fig. 16. Current- Potential.

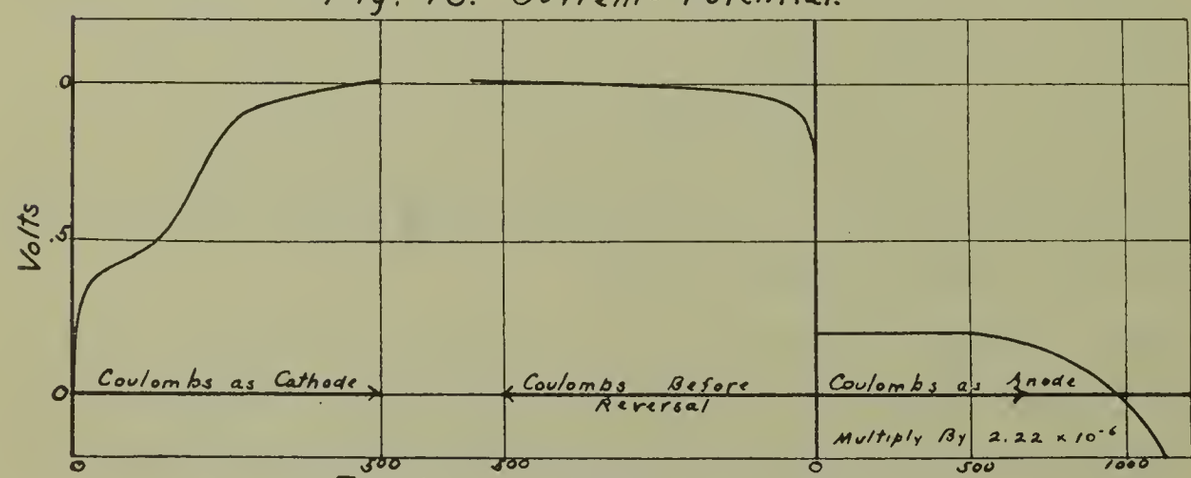


Fig. 17. Coulombs - Overvoltage.

EXP. No. 5.

1.61 volts, so that the curves are incomplete. The significance of the breaks is apparent from the graphical interpretation following.

Current-Potential. Figure 16. From the previous data the potentials have been converted to the basis of the hydrogen electrode. Curve A. Applying the correction method adopted by drawing the line Curve C, parallel to the linear portions of Curve A, the overvoltage is obtained.

Curve B. This is the overvoltage curve for the cycle and in general it conforms to the preceding experiments (except Experiment No. 4.). The fact that the directions of the linear portions of Curve A are the same still further justifies the procedure adopted for ohmic correction. However, since the maximum anodic potentials were not recorded, and since corrosion to lead sulphate is known to take place, it is possible that a second resistance correction curve should be applied on the anodic side, which remains unfinished. This is no doubt due to the presence of the lead sulphate increasing the resistance.

Coulombs-Overvoltage. Figure 17. With the beginning of cathodic current the overvoltage rises from zero to 1.0 volt with two breaks. Either a small amount of lead sulphate or lead oxide is left on the electrode surface at the beginning of the cathodic current. This is no doubt reduced so that a new surface of lead is presented at each cycle. When the reversal to anodic current occurs, the overvoltage falls to 0.2 volt, as the storage of hydrogen is destroyed. This is in accord with previous experiments. In the experiments where corrosion has been found two distinct types have been observed (1) where the lead sulphate leaves the electrode in a stream of fine particles, the electrode surface being apparently clean, and (2) where the lead sulphate adheres to the electrode. In the preceding experiment No. 4 it adhered and in this experiment No. 5 it did not. The nature of the sulphate formation has a bearing on the character of the curves obtained, and this seems to involve the relations of a lead storage cell.

In Figure 17 it is noted that approximately the same number of coulombs is required to remove the hydrogen as is required to build up the maximum overvoltage, or

$500 \times 2.22 \times 10^{-6}$ 1.11×10^{-3} 1.15×10^{-8} Faradays

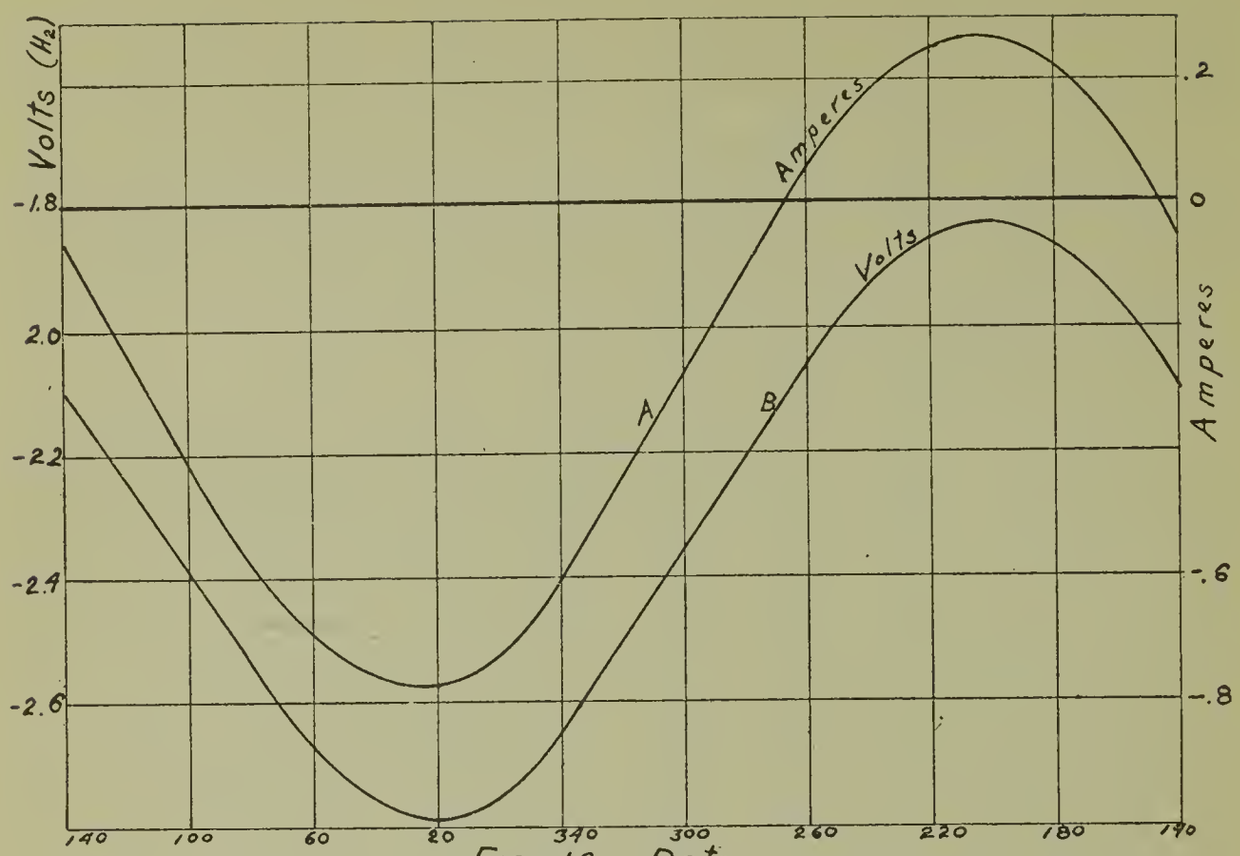


Fig. 18. Data.

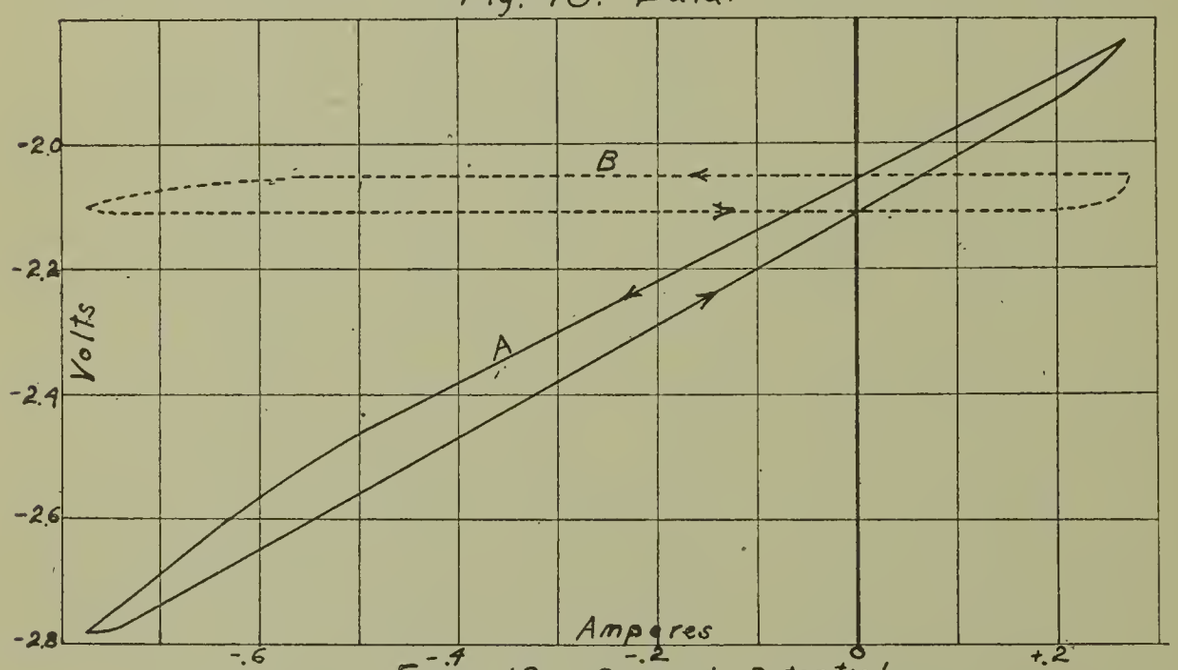


Fig. 19. Current-Potential.

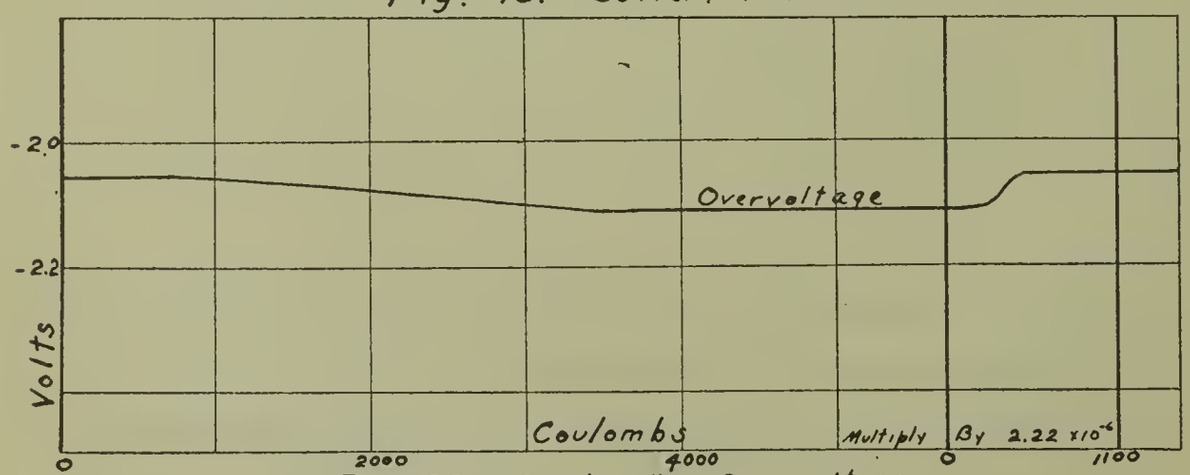


Fig. 20. Coulombs-Overvoltage.

EXP. No. 6.

By calculation of the ratio of atoms of hydrogen to atoms of lead per unit area of electrode these figures have some significance.

Let F = Faradays equivalent of hydrogen on electrode = 1.15×10^{-8}
A = Area of electrode = 2.4 sq. cm. (This is the maximum area of the electrode since it decreased in area by corrosion during the experiment.)
D = Density of electrode = 11.4 gm. per cu. cm.
N = Avogadro's number = 60.6×10^{22} atoms per gram atom.
W = Atomic weight of the electrode = 207
P = Atoms of lead exposed per sq. cm. electrode = $\left(\frac{DN}{M}\right)^{2/3}$
H = Atoms of hydrogen per sq. cm. electrode = FN/A

Then

$$\frac{H}{P} = \frac{F}{A}\left(\frac{NM^2}{D^2}\right)^{1/3} = 2.75$$

As the area (A) and the faradays (F) are quite approximate the nearest approach to a formula for the possible hydride present is $PbH_{2.75}$. As the true area is certainly less than the original area, the ratio will be above 2.75. The order of this ratio rather than the exact numerical value, is the significant point in this calculation as it indicates molecular magnitudes.

Experiment No. 6.

Purpose. To make the reverse current greater than the cathodic current, to study the potential where an oxide film is known to exist.

Conditions. Same as Experiment No. 1. In order to produce this effect electrically, the D. C. connections have been reversed. This makes the delta electrode become a permanent cathode and the alpha and beta electrodes become anodes to it. However each may be considered cathode, in which the period of reversed current is the greater. On this basis the curves have been constructed on the same scale as the preceding experiments. This makes the overvoltage appear as a negative cathodic overvoltage.

Data. Figure 18.

Current-Potential. Figure 19. Curve A. The rising and falling portions of this curve are both linear so that two corrections

have been applied in eliminating ohmic drop. The resultant curve B is the overvoltage. Curve B shows a slight change in potential caused by the reversal of current. Since a film of oxide is present on the electrode, the cathodic current would merely decrease the amount of oxide without otherwise affecting the electrode.

Coulombs-Overvoltage. Figure 20. This shows that the discharge of the anion at lead peroxide takes place at 2.11 volts with reference to the hydrogen electrode. On reversal of the current the change in the electrode potential is about 0.05 volt. The discharge of hydrogen merely removes some of the oxide. This tends to show that the overvoltage or discharge potential is the potential of a film coating on the electrode formed by the current flowing. If such a film is a stable compound little change in potential occurs. The slight drop recorded in this experiment may be due to errors in ohmic correction or to the break down of a higher oxide.

Experiment No. 7.

Purpose. To use intermittently only cathodic current during the cycle, in order to determine the change in potential when no current flows.

Method. The method of experimentation employed in this and the following experiment is somewhat different from the preceding ones. Alternating current is not used, and the synchronous motor is not used. Direct current from a generator is used. It is interrupted by a revolving cylinder which closes the circuit for any desired portion of a revolution. A second cylinder mounted on the same shaft makes contact with the electrode in precisely the same manner as is used by the synchronous motor already described, so that potential measurements can be made for any part of the cycle. Such contact is made for 20 degrees in the cycle compared with 10 degrees in the measurements using alternating current. The speed of the revolving cylinders is variable in this case, whereas in the alternating current experiments the available cycle was necessarily 0.04 second. With this arrangement each cycle consists of two periods, (a) a period of

activity where current flows, (b) a period of rest where no current flows. Measurements are made against the calomel cell.

Data.

Normal sulphuric acid electrolyte
Calomel electrode (normal)
Lead cathode, area 1 sq. in. (6.45 sq. cm.)
Current, 0.75 ampere (instantaneous, not average)
Period of activity
A : 58 percent cycle
B : 37 percent cycle
C : 12 percent cycle
Cycle, 0.04 second or 1500 R. P. M.

Figure 21. This figure shows data of cycles A, B, and C with current flowing during the blank portion of the cycle. The potential against the calomel electrode is shown only for the period of rest. With the same current density is each case more coulombs pass per cycle in A than C. The decreasing potential curve breaks off with current at about 1.4 volts which may be taken as the potential at the time current stops. This converted to the hydrogen electrode is about 1.1 volts, and compares with the hydrogen overvoltage obtained by the first method. Comparison of the three curves shows that the most rapid drop in potential occurs in the cycle A which has the greatest period of activity. No explanation is offered for this at this point.

Experiment No. 8.

Purpose. To decrease the frequency of interrupted current.

Conditions. Same as Experiment No. 7, using 12 percent period of activity.

Data. Figure 22. Speed of apparatus: A 1630 R. P. M.; B 1150 R. P. M.; C 730 R. P. M. Figure 22 shows the fall of potential during the period of rest. As the time of each period is different, the same curves have been plotted against time in Fig. 23. Curves for 1150 and 730 R. P. M. are almost identical, indicating the velocity of depolarization by time. The curve for 1630 R. P. M. shows a greater velocity. This is perhaps because the frequency being greater and the period of activity shorter, time of activity is not great enough to give saturation of the electrode. A calculation from the data by the formula developed in Experiment 5, shows that sufficient hydrogen is discharged in

the period of activity to just give PbH_3. This shows that this is almost a limiting case. It is further interesting to note that the curve for 730 R. P. M. was duplicated with and without mechanical agitation of the electrolyte in the cell. This shows that diffusion through the electrolyte plays no role in the depolarization.

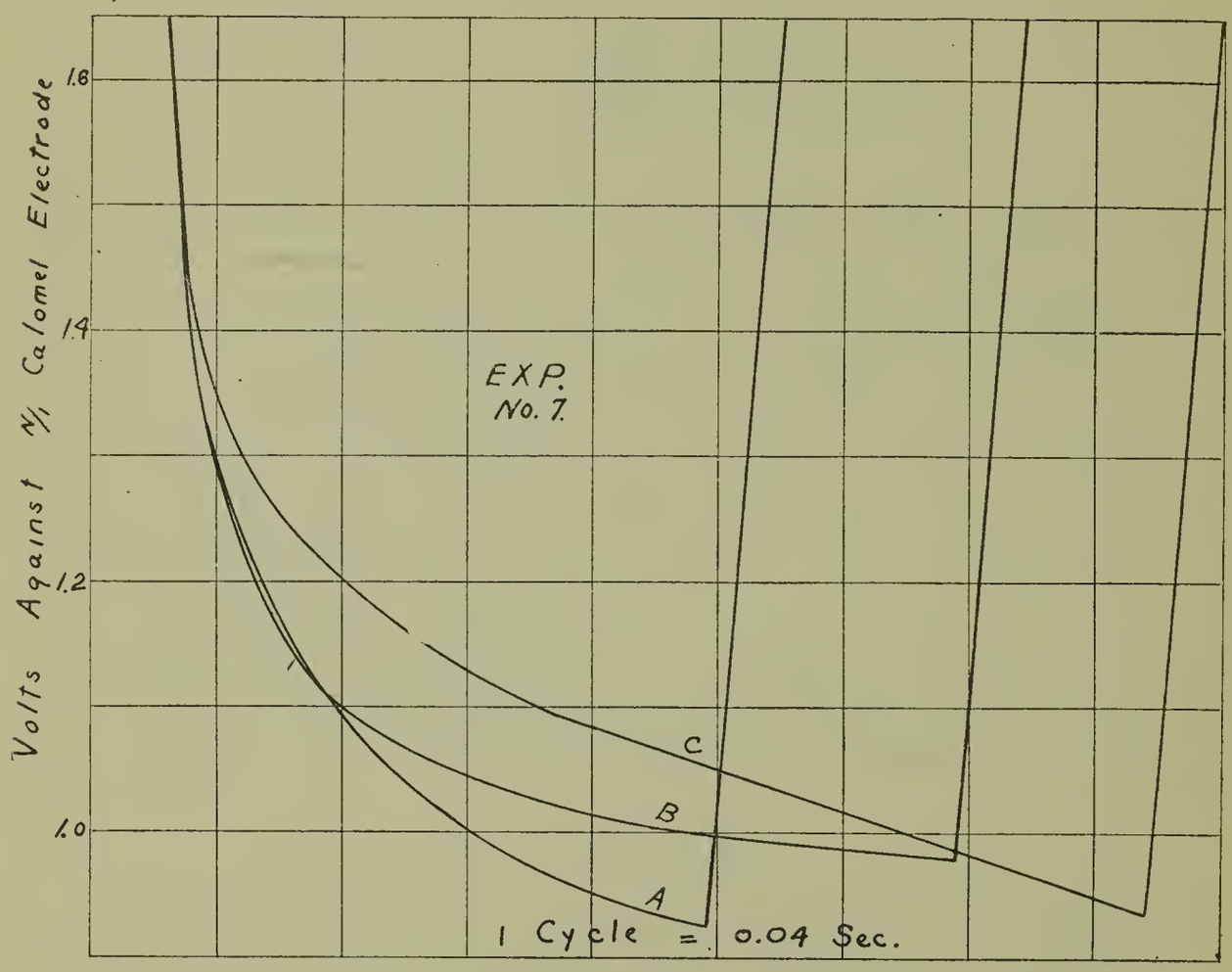


Fig. 21. Effect of Increasing Period of Activity.

VI. DISCUSSION OF RESULTS.

1. *Summary of Alternating Current Experiments.* The experiments above reported have covered all the cases of changing relationship between alternating current and direct current without a regard for current density. The latter is an impossible consideration except to maintain the direct current density constant. This has been done. The introduction of the sine wave nullifies the value or significance of amperes. It has been found that c o u l o m b s is the best variable in which to summarize the results. Experiment 4 as described and represented by Figure 14

is perhaps doubtful, since it is at variance with the other experiments recorded. Although the reason for this has not been investigated, it is no doubt due to the nature of the corrosion. Attempts to duplicate conditions of this experiment were not successful as variations in the direct current amperes caused by the corrosion was a disturbing factor. Although not noticed when carried out, a change may have occurred when measurements were taken. Although corrosion also occurred in Experiment No. 5 with alternating current alone, the nature of the sulphate formation was different. Experiment No. 5 shows the same phenomena as those in which no corrosion took place.

TABLE IV.

1 Exp. No.	2 Max. Cathodic Amp.	3 Max. Anodic Amp.	4 Max. Overvol. Attained.	5 Cath. Coul. per Cycle x 10^4	6 Anod. Coul. per Cycle x 10^4	7 *
1	0.41	—0.10	1.11	103	0	4
2	0.58	—0.05	1.02	109	2.2	6
3	0.71	0.165	0.93	121	12.9	9
4	1.02	0.51	(0.73)	155	49	12
5	0.55	0.55	1.00	59	59	15
6	0.27	0.775	—2.10	21.3	124	18

* No. of figure from which coulombs were measured by a planimeter.

In Figure 24 the horizontal lines cross the vertical axis at points corresponding to the maximum overvoltage attained (column 4). The length of the line to the right corresponds to the cathodic coulombs (column 5). The length of the line to the left corresponds to anodic coulombs (column 6). The line for the doubtful experiment is dotted, since a constant maximum overvoltage was not attained.

2. *General Discussion.* The evidence of these experiments indicates a chemical compound formed as a film over the electrode. As anode a film is known to exist, which is the stable peroxide. By a reverse current upon this film, less than 0.1 volt change is made in the potential. This change may be error in interpretation of

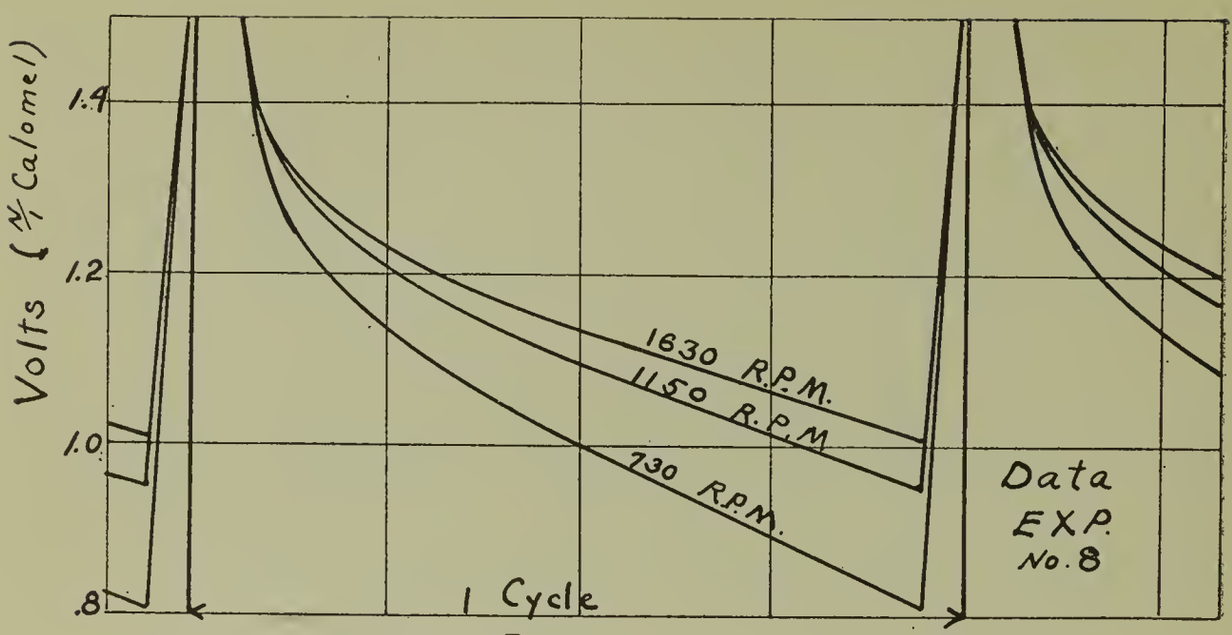


Fig. 22. Effect Frequency on Back E. M. F.

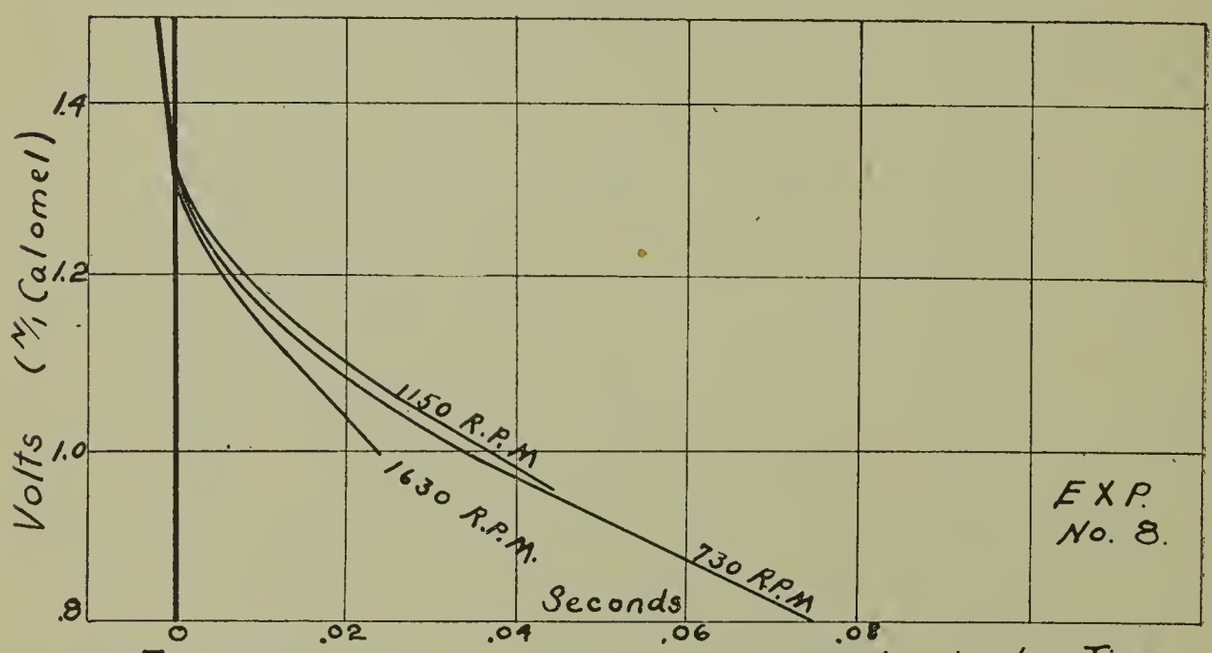


Fig. 23. Depolarization of Electrode by Time.

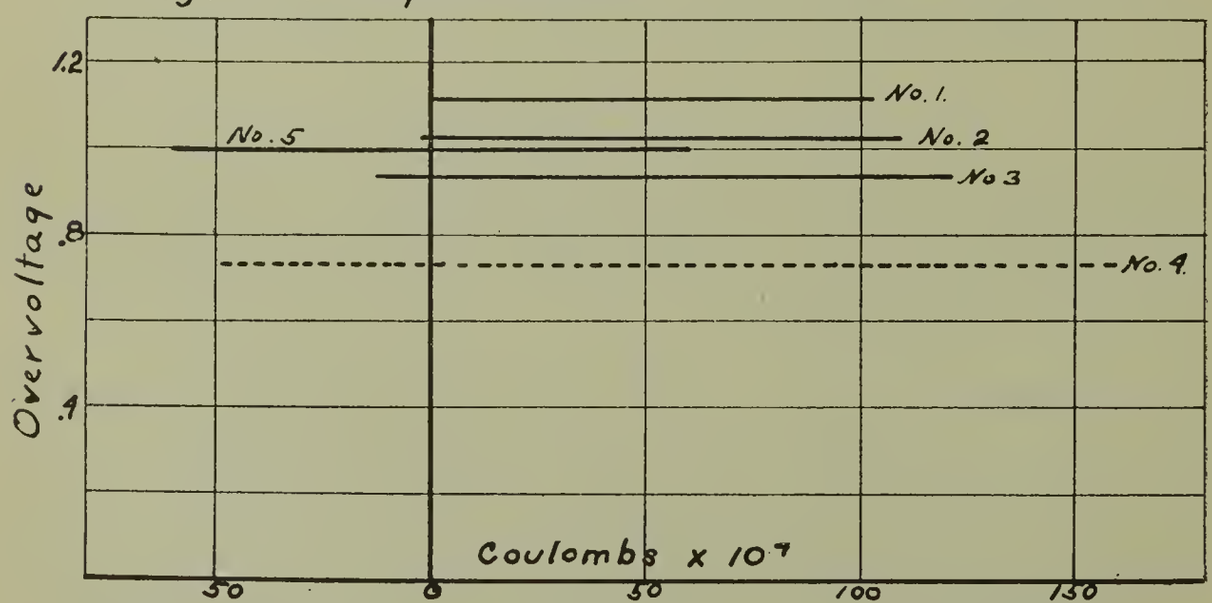


Fig. 24. Summary of Maximum Overvoltages.

results, or it may be the change from a higher oxide to the stable one. The method employed is not sensitive enough to distinguish the difference. As to the hydride film, its existence is indicated by a similar behavior of the potential curve. Reverse current lowers the potential to a constant value found to exist in three independent experiments, each experiment covering over 100,000 repeating cycles. This must correspond to a fairly stable hydride. The change in potential is greater because of the probable instability of the higher hydrides. In general sufficient coulombs of cathodic current at least to equal the coulombs of reverse current are required to restore the maximum overvoltage.

When continuous direct current alone flows, the depth of the film probably increases. It is indicated by the fact that as the reverse coulombs are increased the maximum overvoltage is somewhat lowered. When sufficient reverse current flows to remove all the hydride film, a new surface of lead becomes exposed in each cycle. Assuming that the hydrogen is discharged and forms a hydride with the lead, it will only cause a maximum overvoltage when at least a molecular film is formed. Experiment No. 5, Figure 17, shows that the coulombs equivalent of hydrogen removed from the electrode by the reverse current, and the coulombs of hydrogn to saturate it, are approximately the same. Assuming the film to be of molecular order it corresponds to a formula of PbH_3 roughly. This is of significance because of its magnitude.

The experiments carried out with intermittent current show the rate of decomposition of hydrides formed. When the current which maintains them is removed, they drop rapidly and then fall to a lower value more gradually. The decomposition of the hydrides with intermittent current would give lead and hydrogen, the escape of which would affect the surface. The decomposition of the hydrides by reverse current would give lead and hydrogen ions. In both cases lower hydrides may be intermediate products. The chief point is that the former case would give a disruptive effect, which would be absent in the latter. The greater the amount of hydride present, the greater this disruptive effect

would be. This explains why in Figure 21 the potential falls more rapidly with increased period of activity.

As to the mechanism of the discharge of hydrogen ions, there are evidently two conditions under which it takes place, first, while the overvoltage is building up; second, after the maximum overvoltage has been attained. It might be stated that the increasing overvoltage is due to the increasing concentration of monatomic hydrogen on the surface, which eventually becomes saturated at the maximum overvoltage. Assume that such is the case.

Then the formation of monatomic hydrogen on the electrode builds up an increasing concentration, at the same time increasing the rate of formation of molecular hydrogen. Up to the maximum overvoltage the total hydrogen discharged has either gone to molecular hydrogen, or is still present as monatomic hydrogen on the electrode. The latter is probably the smaller amount. But the results show that only approximately three hydrogen ions are discharged per atom of surface of lead up to the maximum overvoltage. If a portion of this has gone to molecular hydrogen, that which remains as monatomic hydrogen would be less than the ratio 3 to 1, and seemingly too small to support the assumption. The ratio is more favorable to the hydride theory.

This theory would indicate that the first discharge of H ions forms a hydride, either by direct union of the charged Pb atoms with the H ions, or by reaction of the monatomic hydrogen with the lead molecules. After the complete film of hydride is formed, it decomposes in equilibrum with the current flow, or is maintrained by the latter so that the excess hydrogen escapes as molecular hydrogen. Referring to data which the author hopes to present in a subsequent paper (in which similar studies are made in the presence of depolarizers), it may be stated that the presence of a depolarizer flattens the coulombs-overvoltage curve, so that eight to ten times as many coulombs are required to reach the vicinity of the maximum overvoltage, at the same time removing the sharp knee in the curve without a depolarizer. Such a curve would be obtained in these experiments were the overvoltage caused by the monatomic hydrogen and not by a hydride film.

VII. SUMMARY.

Potentiometer measurements of the potential difference of a lead cathode and a hydrogen electrode have been made over a cycle of 0.04 second, during which combined alternating and direct currents flow through the electrode. This potential has been plotted against the current flowing, and a graphic correction made for the true overvoltage. When plotted against coulombs, interesting results are found. These indicate the formation of stable and unstable compounds, as films on the electrode, as the cause of overvoltage.

Measurements with intermittent direct current give the approximate stability of the lead hydride when the current is cut off. The potential of the hydride drops in this case about 0.6 volt in 0.08 second. Indications are that there is a lower hydride that is quite stable. An approximate calculation of the higher hydride formula gives about PbH_3.

The maximum overvoltage attained during cathodic action is only slightly lowered by superimposing increasing amounts of alternating current upon the direct current.

The author regrets that this work is not more complete in some details. A second paper, covering the same work in the presence of depolarizers, confirms the results of this paper. The present indications are that no more work will be done.

The author wishes to extend his thanks to Dr. D. F. Calhane of the Worcester Polytechnic Institute, who inspired the initial interest in this subject, and to the Research Laboratory of the National Aniline and Chemical Co., Inc., for the excellent facilities and opportunity provided for the experimental work of this paper, and to Dr. E. K. Strachan of the Laboratory for many valuable suggestions.

DISCUSSION.

Colin G. Fink[1]: Mr. Jones' reference to the formation of films on his lead electrodes is a subject of very great importance.

[1] Consulting Electrometallurgist, New York City.

I had occasion to refer briefly to it at the last meeting of the Society in connection with the paper on lead-thallium alloys. It is very peculiar, or perhaps very natural, that lead will form different films, depending upon the impurities present in the lead of the anode. In most cases you get a lead peroxide film, and not a lead sulphate film. But this subject is to be investigated more fully, and I trust that at the next meeting we will have a paper from Dr. Bancroft reporting upon his tests at Cornell.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 28, 1922, President Acheson Smith in the Chair.

CONDUCTIVITY OF COPPER REFINING ELECTROLYTES.[1]

By Edward F. Kern[2] and M. Y. Chang.[2]

Abstract.

The specific conductivities of solutions of sulphuric acid, copper sulphate, and of mixtures of sulphuric acid and copper sulphate were determined at 25° C., 40° C., and 55° C. The concentrations of the solutions were 5, 10, 15, and 20 grams per 100 cc. Tables and curves are given for the several series of solutions, and for the different temperatures. The effects of the presence of arsenic, nickel sulphate, and ferrous sulphate upon the conductivity of a copper-refining electrolyte were determined, showing that the presence of arsenic does not appreciably depress the conductivity, whereas the presence of nickel sulphate and of ferrous sulphate depress the conductivity very much.

In the refining of metals by electrolysis the influence of the conductivity of the electrolyte upon the power consumption is of greatest importance. It is evident that the higher the conductivity of the electrolyte the less will be the power consumed in order to refine a given amount of metal.

The usual means of raising the conductivity of an electrolyte are: (a) by using a more concentrated solution; (b) by adding to the electrolyte a certain amount of highly ionized materials, which are not a hindrance to the dissolving of the anode nor to the formation of satisfactory cathode deposits; (c) by heating the electrolyte; (d) by preventing the accumulation in the electrolyte of materials which reduce the conductivity.

The object of determining the conductivities of the various

[1] Manuscript received March 8, 1922.

[2] Department of Metallurgy, School of Mines, Columbia University, New York City.

solutions, which are reported in this article, was to obtain data which would be useful in the selection of the most economical mixtures of sulphuric acid and copper sulphate for use in the electrolytic refining of copper, and to determine the effect of the presence of the commoner impurities which accumulate in the electrolyte in the process of the refining, the commoner impurities being nickel and arsenic, and possibly under certain conditions also iron. These determinations were made following the suggestions of Mr. F. R. Pyne, U. S. Metals Refining Co., Chrome, N. J.

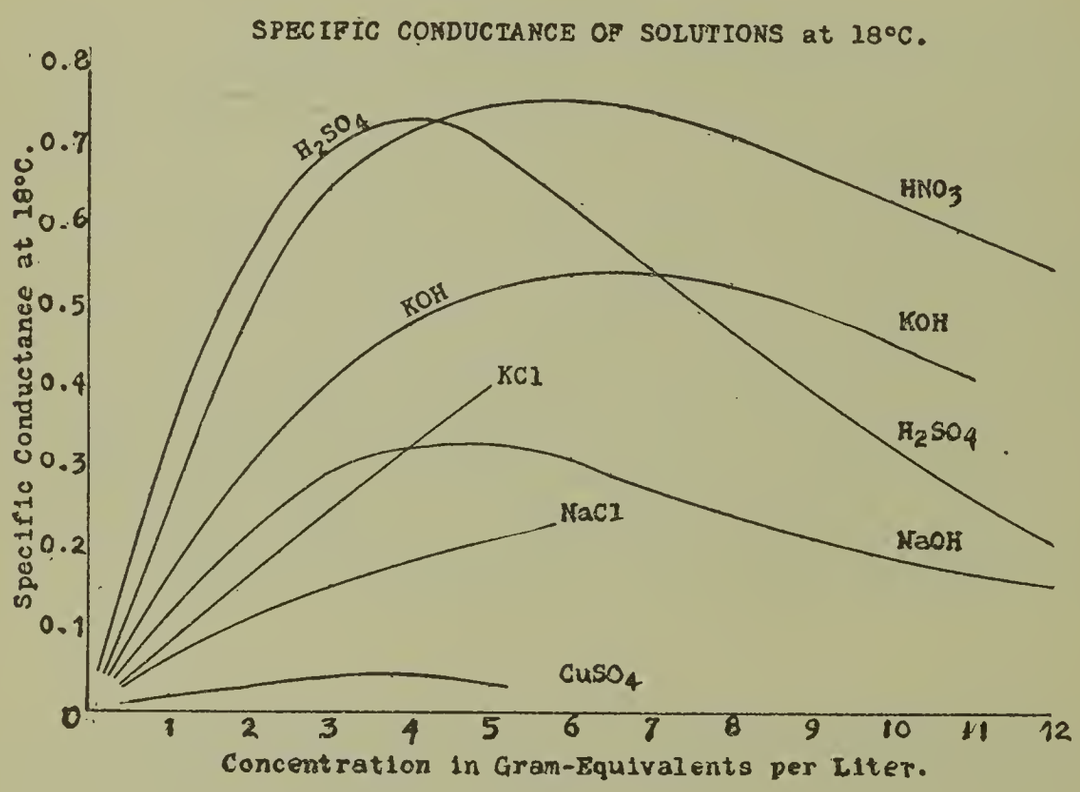


FIG. 1

The general effect of concentration of a solution upon the specific conductivity (L) is illustrated by Fig. 1., which shows an increase up to a maximum point after which a further increase in concentration gives a decrease in specific conductance. (Allmand "Principles of Applied Electrochemistry" 1920 Ed., p. 65). The specific conductivity of an electrolyte varies with the temperature, and is expressed for temperatures below 100° C., by the equation:

$$L_t = L_{18} [1 + c (t - 18)].$$

The increase in conductivity of an electrolyte with increase in temperature is due to the decrease in the internal friction of the

solvent, which permits the ions to move more rapidly, thus causing an increase in the conductivity. "As the viscosity of water decreases rapidly with increasing temperature, the "fluidity" (reciprocal of the viscosity) increases. This rate of increase is about the same as the rate at which conductivity increases, so that the decreased resistance of electrolytes nearly parallels the decrease in resistance to flow of water. Hence it is very probable that the increase in conductivity is largely due to the decrease in resistance to the motion of ions through water." (Millard "Physical Chemistry for Colleges" 1921 Ed., p. 179).

Richardson and Taylor determined the specific conductivities of a series of solutions of sulphuric acid, copper sulphate, and mixtures of sulphuric acid and copper sulphate, at 25°C. and 45°C. (Trans. Am. Electrochemical Soc., 1911, **20,** 179). Their results are given in Table I. The conclusions from the results of their determinations were as follows: First. Addition of copper sulphate to solutions of sulphuric acid: (a) Increases the conductivty of the mixture if the sulphuric acid is less than 3 grams per 100 cc.; (b) Has no effect on the conductivity of the mixture if the sulphuric acid is 3 grams per 100 cc.; (c) Decreases the conductivity of the mixture if the sulphuric acid is over 3 grams per 100 cc. Second. The temperature coefficient of mixtures of equal parts of copper sulphate and sulphuric acid appears to be that of the sulphuric acid alone. The average temperature coefficient expressed in percentage per degree centigrade is: for copper sulphate solutions 1.71 percent; for sulphuric acid solutions 1.05 percent; and for mixtures of copper sulphate and sulphuric acid solutions 0.97 percent. Third. The probable error of the determinations is less than 0.5 percent.

Goodwin and Horsch determined the specific conductivities, at 25°C., of solutions saturated with $CuSO_4 . 5H_2O$ and containing free sulphuric acid ranging from 0.15 to 3.67 gram-equivalent per liter (0.73 to 17.93 grams free H_2SO_4 per 100 cc.) The solubility of $CuSO_4 . 5H_2O$ in these varying strengths of free sulphuric acid, and the specific gravities of the resulting solutions, are also given. The results are given in Table II. The conclusions drawn from

Table I

Richardson and Taylor's Results

Conductivity Expressed in Reciprocal Ohm per Centimeter Cube (Specific Conductivity)

Temperature		25°C.				
Grams of H_2SO_4 per 100 cc.		0	5	10	15	20
Grams of $CuSO_4.5H_2O$ per 100 cc.	0	.....	0.208	0.410	0.565	0.683
	5	0.0153	0.204	0.388	0.531	0.646
	10	0.0221	0.195	0.350	0.500	0.600
	15	0.0348	0.189	0.338	0.458	0.558
	20	0.0423	0.182	0.319	0.433	....
Temperature		45°C.				
Grams of H_2SO_4 per 100 cc.		0	5	10	15	20
Grams of $CuSO_4.5H_2O$ per 100 cc.	0	.....	0.246	0.492	0.683	0.839
	5	0.0205	0.242	0.461	0.643	0.791
	10	0.0294	0.222	0.422	0.606	0.738
	15	0.0468	0.217	0.381	0.545	0.690
	20	0.0574	0.212	0.378	0.521	0.643

Table II.

Goodwin and Horsch's Results.

Specific Conductivity, and Specific Gravity, of Saturated Solutions of Copper Sulphate in Varying Concentrations of Sulphuric Acid

Temperature of Solutions °C.	Concentration of Solutions				Density Referred to Water	Specific Conductance in Mho
	Gram-equivalent per Liter		Grams per 100 cc.			
	Free H_2SO_4	$CuSO_4$	Free H_2SO_4	$CuSO_4.5H_2O$		
25.00	.....	2.818	.....	35.163	1.2140	0.05555
25.00	0.1488	2.784	0.7291	34.740	1.2105	0.06884
25.00	0.4208	2.634	2.0619	32.867	1.2070	0.09845
25.00	0.8680	2.457	4.2532	30.659	1.2115	0.1458
25.00	1.345	2.320	6.5905	28.950	1.2130	0.2023
25.01	1.876	2.181	9.1924	27.215	1.2165	0.2608
25.00	1.914	2.153	9.3786	26.866	1.2162	0.2671
25.02	3.077	1.837	15.0773	22.923	1.2229	0.4005
25.01	3.659	1.649	17.9291	20.577	1.2267	0.4596

their experiments are: (1) The solubility of $CuSO_4 . 5H_2O$ in sulphuric acid solutions decreases with the increase in free sulphuric acid. (2) The specific conductivity of saturated solutions of copper sulphate in solutions containing free sulphuric acid increases with increase of the free sulphuric acid, the increase in specific conductivity of these solutions being a straight line function. (Chemical and Metallurgical Engineering, 1919, **21,** 182).

EXPERIMENTAL PART.

Two standardized stock solutions were prepared; one contained 99.98 grams H_2SO_4 per 100 cc.; and the other contained 6.365 grams copper (24.98 grams $CuSO_4 . 5H_2O$) per 100 cc. Measured amounts of these solutions were taken and diluted to the required volume to produce solutions containing the amounts of free sulphuric acid, copper sulphate, and mixtures of free sulphuric acid and copper sulphate, as given in Tables III and V. The solutions which contained 135 grams of free H_2SO_4, 35 grams of copper (137 grams $CuSO_4 . 5H_2O$), and different amounts of arsenic, nickel, and iron, were prepared by adding a weighed amount of either arsenic oxide, nickel sulphate, or ferrous sulphate to a measured amount of a mixture of the standardized stock solutions, and diluting to the required volume so as to produce the series of solutions which are recorded in Tables IV and V.

The conductivities of the solutions were determined by using a Leeds and Northrup Conductivity Set, which is described in their Catalogue No. 48 (1919), the alternating current being supplied by one of their constant speed high frequency generators (1,000 cycles per second). The cell in which the measurements were made was a Washburn cell, Type C. It was standardized by means of a normal solution of potassium chloride, the specific conductivity of which had been accurately determined. The cell constant (C) was determined for each temperature at which the determinations were made, by using the specific conductivity values of normal KCl solution (74.56 grams KCl per liter), as follows:

L at 18° C. = 0.09827 mho.
L at 25° C. = 0.11157 mho.
L at 40° C. = 0.14007 mho.
L at 55° C. = 0.16857 mho.

TABLE III.

Specific Conductivity of Solutions of Sulphuric Acid, Copper Sulphate, and of Solutions Containing Free Sulphuric Acid and Copper Sulphate.

Conductivity Expressed in Reciprocal Ohm per Centimeter Cube.

Temperature of Solutions 25° *C.*

Grams of Free H_2SO_4 per 100 cc.		0	5	10	15	20
Grams of $CuSO_4.5H_2O$ per 100 cc.	0	.....	0.2165	0.4069	0.5559	0.6684
	5	0.0148	0.1977	0.3714	0.5123	0.6195
	10	0.0252	0.1868	0.3480	0.4815	0.5729
	15	0.0333	0.1772	0.3214	0.4392	0.5256
	20	0.0402	0.1750	0.3017	0.4087	0.4852

Temperature of Solutions 40° *C.*

Grams of Free H_2SO_4 per 100 cc.		0	5	10	15	20
Grams of $CuSO_4.5H_2O$ per 100 cc.	0	.....	0.2490	0.4722	0.6498	0.7901
	5	0.0191	0.2233	0.4272	0.6016	0.7433
	10	0.0320	0.2096	0.3989	0.5619	0.6792
	15	0.0425	0.1992	0.3688	0.5135	0.6263
	20	0.0517	0.1956	0.3486	0.4807	0.5810

Temperature of Solutions 55° *C.*

Grams of Free H_2SO_4 per 100 cc.		0	5	10	15	20
Grams of $CuSO_4.5H_2O$ per 100 cc.	0	.....	0.2751	0.5262	0.7312	0.8981
	5	0.0229	0.2418	0.4740	0.6731	0.8339
	10	0.0382	0.2250	0.4394	0.6313	0.7733
	15	0.0510	0.2135	0.4055	0.5765	0.7144
	20	0.0623	0.2059	0.3835	0.5403	0.6643

The values for L at 40° C. and 55° C. were calculated by using the temperature coefficient of N.KCl solutions, which is 0.0193, or 0.0019 mho per degree centigrade. (Lehfeldt "Electrochemistry," 1918 Ed., p. 55.) The cell constant (C) should be determined for each temperature at which it is used, as this constant (C) changes with change of temperature, owing to linear expansion of the platinum electrodes and connections, and to the cubical expansion of the glass cell.

Table IV.

Effect of the Presence of Arsenic, Nickel Sulphate, and Ferrous Sulphate Upon the Conductivity of a Copper Refining Electrolyte Containing 135 Grams Free Sulphuric Acid and 35 Grams of Copper (137 Grams $CuSO_4.5H_2O$) Per Liter of Solution.

Conductivity Expressed in Reciprocal Ohms per Centimeter Cube.

Temperature of Solutions 25° C.

Grams of Impurities Per Liter	Effect of Presence of		
	Arsenic	Nickel	Iron
0	0.4094	0.4094	0.4094
10	.....	0.3827	0.3726
20	0.4014	0.3595	0.3424
30	0.3981	0.3379	.....
40	0.3948	.....	.....

Temperature of Solutions 40° C.

Grams of Impurities Per Liter	Effect of Presence of		
	Arsenic	Nickel	Iron
0	0.4766	0.4766	0.4766
10	.....	0.4463	0.4345
20	0.4708	0.4202	0.4003
30	0.4670	0.3956	.....
40	0.4621	.....	.....

Temperature of Solutions 55° C.

Grams of Impurities Per Liter	Effect of Presence of		
	Arsenic	Nickel	Iron
0	0.5307	0.5307	0.5307
10	.....	0.4980	0.4834
20	0.5265	0.4688	0.4469
30	0.5231	0.4440	.....
40	0.5194	.....	.....

The determination of the cell constant (C) is illustrated by the following example: The cell was filled with N.KCl solution, its temperature was brought to exactly 25°C., and the resistance of the solution in the cell was determined; in one case it gave the

TABLE V.

Effect of Temperature Upon the Conductivity of Solutions of Sulpuhric Acid, Copper Sulphate, Copper Sulphate and Free Sulphuric Acid, and Copper Refining Electrolytes Containing Varying Amounts of Nickel as Sulphate.

Conductivity Expressed in Reciprocal Ohm per Centimeter Cube.

Grams per 100 cc. of Solution	Specific Conductivity at		
	25°C.	40°C	55°C.
20 grams H_2SO_4.....	0.668 mho	0.790 mho	0.898 mho
15 grams H_2SO_4.....	0.555 mho	0.650 mho	0.731 mho
13.5 grams H_2SO_4	0.515 mho	0.597 mho	0.670 mho
13.5 grams free H_2SO_4..... 13.7 grams $CuSO_4.5H_2O$.....	0.409 mho	0.477 mho	0.531 mho
13.5 grams free H_2SO_4..... 13.7 grams $CuSO_4.5H_2O$..... 1 gram nickel.....	0.383 mho	0.446 mho	0.498 mho
13.5 grams free H_2SO_4..... 13.7 grams $CuSO_4.5H_2O$..... 2 grams nickel	0.360 mho	0.420 mho	0.469 mho
13.5 grams free H_2SO_4..... 13.7 grams $CuSO_4.5H_2O$..... 3 grams nickel	0.338 mho	0.396 mho	0.444 mho
20 grams $CuSO_4.5H_2O$.....	0.040 mho	0.052 mho	0.062 mho
13.7 grams $CuSO_4.5H_2O$.....	0.033 mho	0.040 mho	0.049 mho
10 grams $CuSO_4.5H_2O$.....	0.025 mho	0.032 mho	0.038 mho

resistance of the solution in the cell as 771.01 ohms, the reciprocal of which (1/771.01) is 0.001297 mho. The constant (C) was then calculated by dividing the specific conductance of N.KCl solution at 25° C. by 0.001297, which is: $\frac{0.11157}{0.001297} = 86.10$

As an illustration of the procedure of calculating the specific conductance (L) of the various solutions which were determined, the two following examples are given:

(1) Solution containing 5 grams of sulphuric acid per 100 c.c.

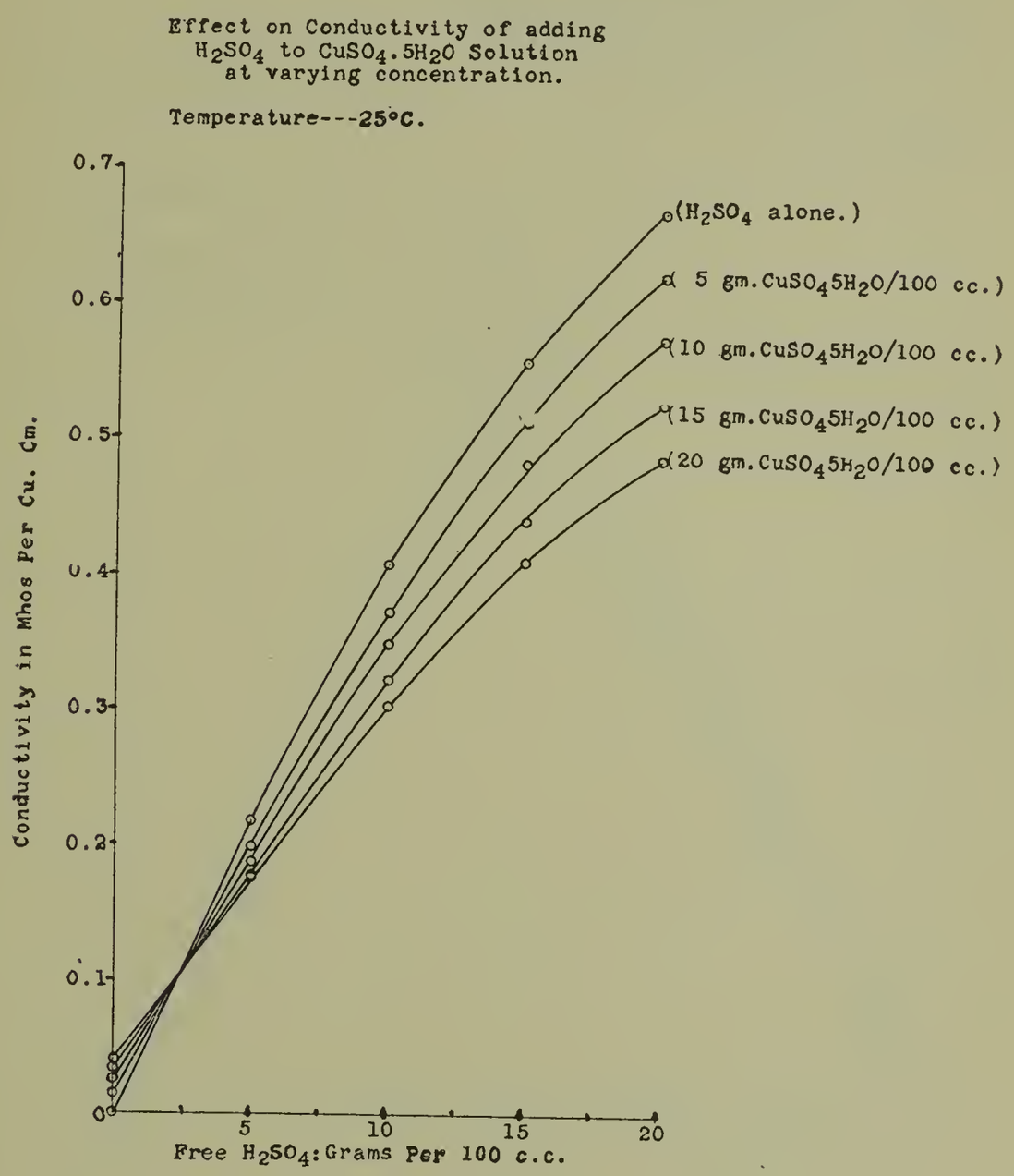


FIG. 2.

The conductivity of this solution in the cell at 25° C. was found to be 0.002516 mho; so $L = (0.002516 \times 86.1) = 0.2166$ mho.

(2) Solution containing 135 grams free H_2SO_4 and 35 grams of copper per liter. The conductivity of this solution in the cell at 25° C. was found to be 0.004755 mho; by multiplying this by 86.1 we obtained 0.4094 mho as its specific conductance.

The results of the determinations of the specific conductivities of the solutions are given in Tables III, IV and V; these were plotted, producing the curves shown by Figs. 2, 3, 4, 5, 6, 7 and 8.

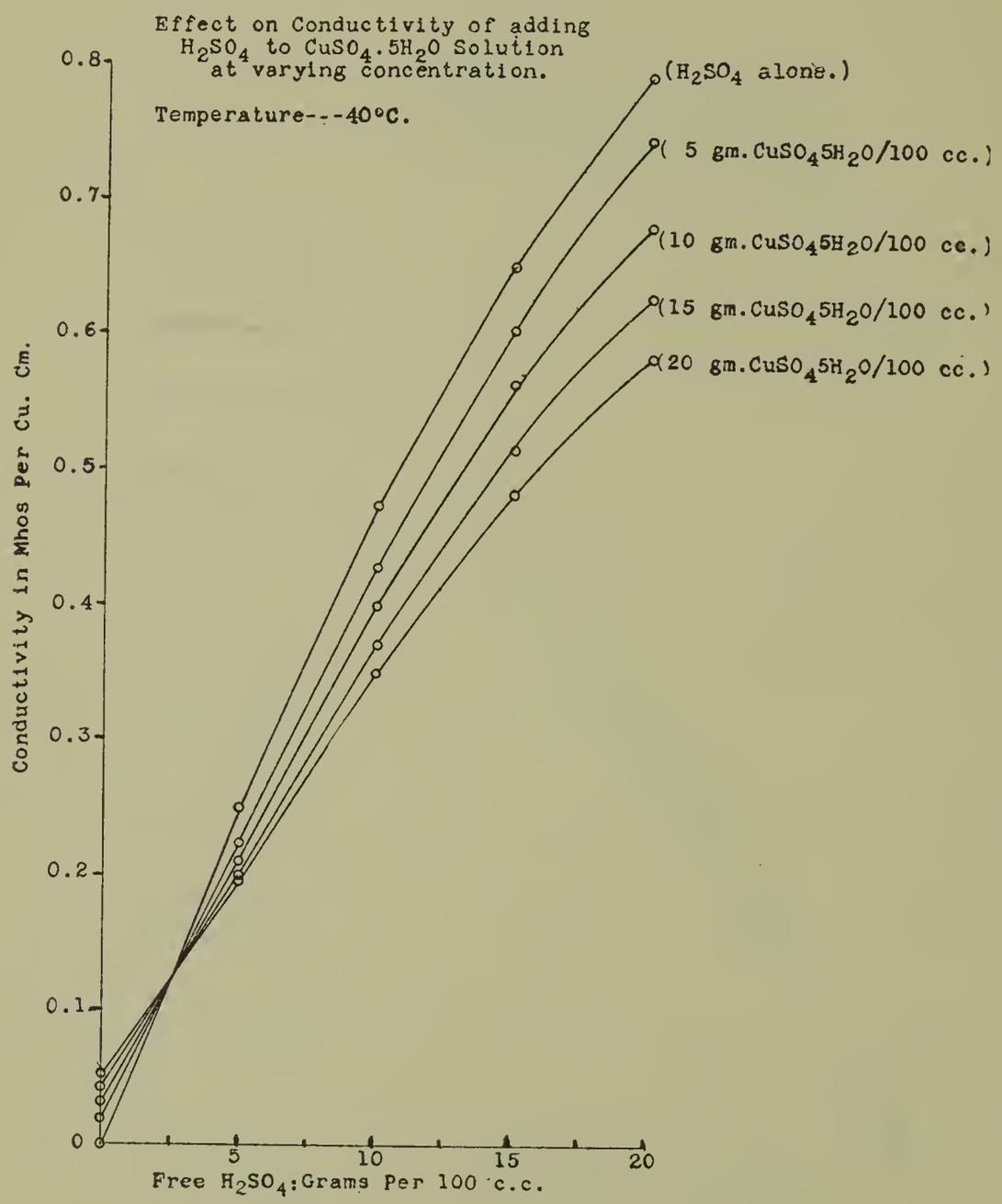


FIG. 3.

SUMMARY OF RESULTS

1. Copper sulphate solutions are poor conductors of electricity, and their conductivity is not much increased by raising the temperature.

2. Sulphuric acid solutions are good conductors of electricity, and with rise in temperature their conductivity increases rapidly.

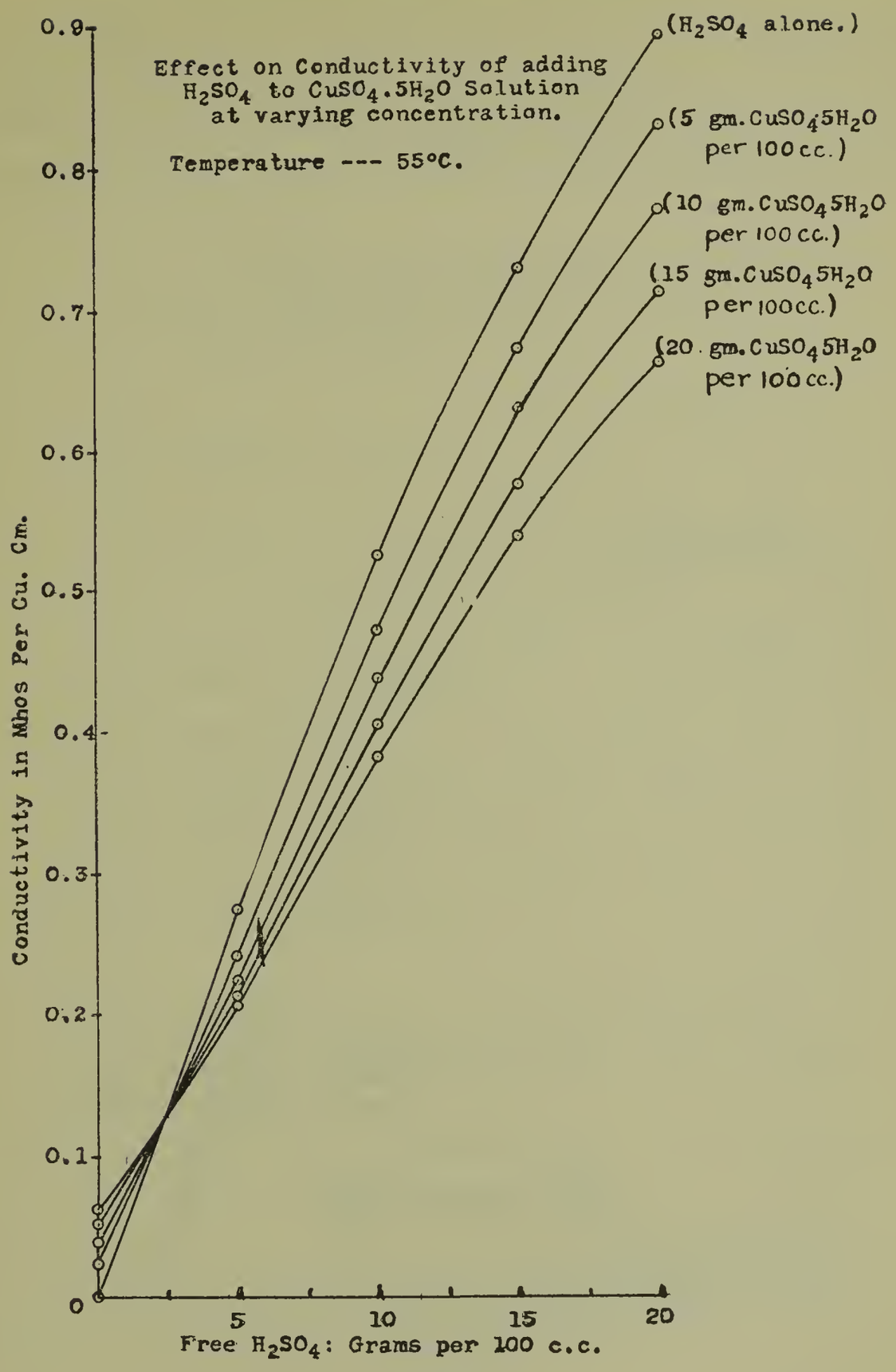


FIG. 4.

3. The addition of sulphuric acid to copper sulphate electrolytes greatly increases the conductivity of the resulting solution.

4. The addition of copper sulphate to sulphuric acid solutions (a) increases the conductivity of the resulting mixture if the free

sulphuric acid content is less than about 2.5 grams per 100 cc.; and the higher the temperature of the solution the greater is the relative increase in the conductivity; (b) does not have any effect upon the conductivity of the resulting solution if the free sulphuric

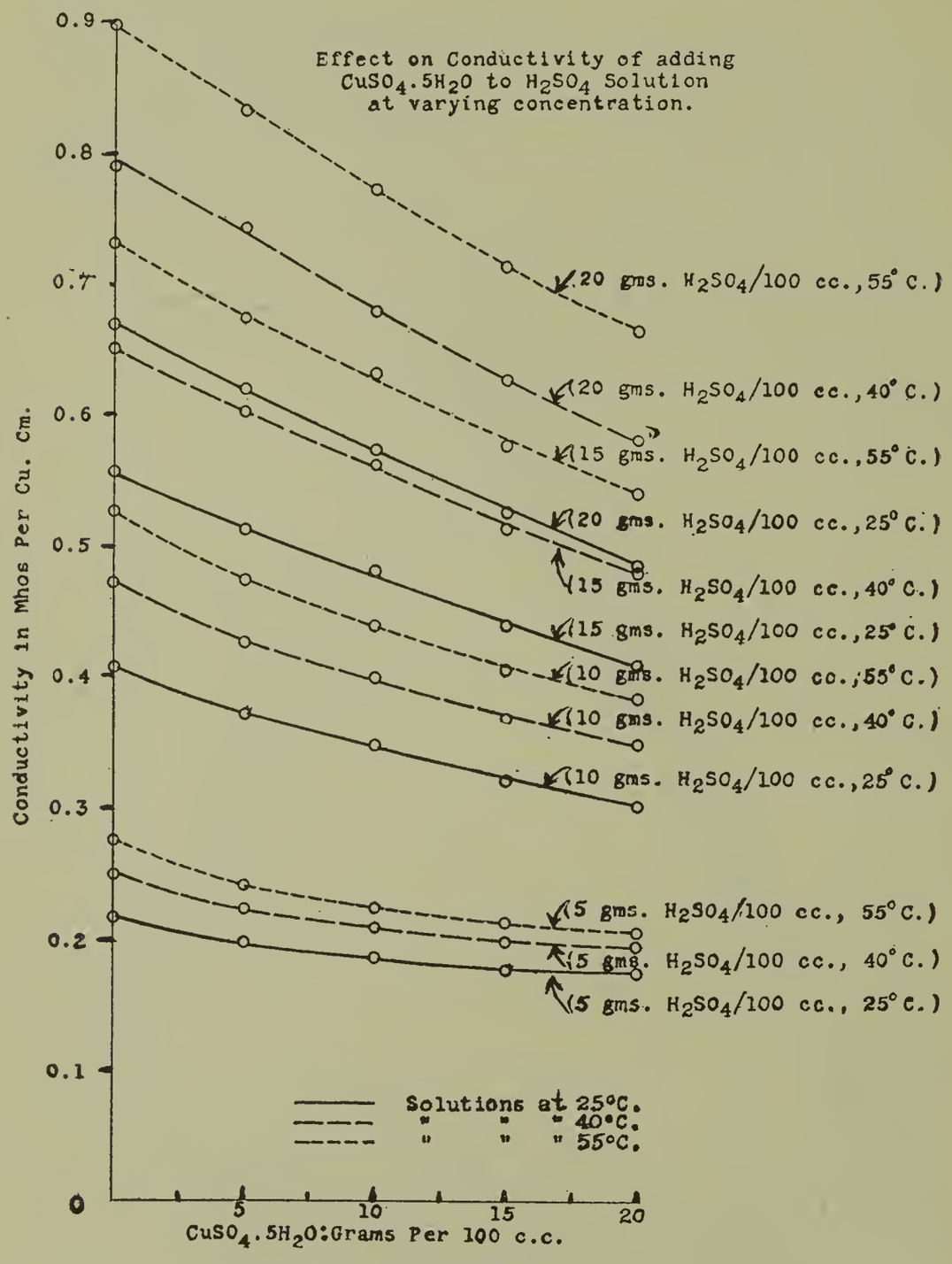


FIG. 5.

acid content is approximately 2.5 grams per 100 cc.; (c) decreases the conductivity of the resulting solution if the free sulphuric acid content is more than about 2.5 grams per 100 cc.; and the higher the temperature of the resulting solution the greater is the relative decrease in the conductivity.

5. The temperature coefficient is different for different concentrations of sulphuric acid, copper sulphate, and for different concentrations of mixtures of free sulphuric acid and copper sulphate; it must be determined for each solution and for the various concentrations.

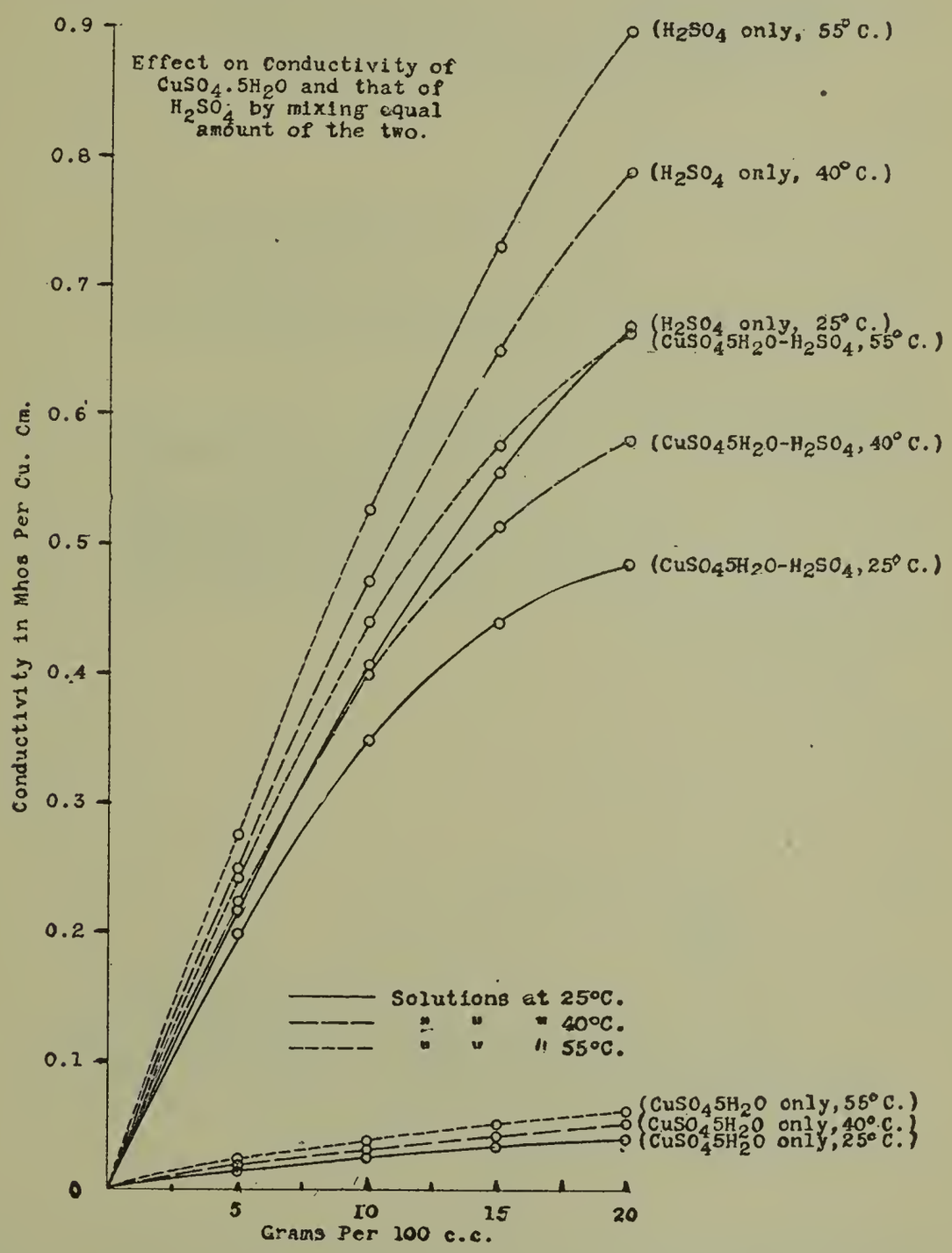


FIG. 6.

6. The addition of arsenic to copper refining electrolytes slightly decreases their conductivity. The addition of 20 grams of arsenic per liter of solution containing 135 grams of free sulphuric acid and 35 grams of copper (137 grams $CuSO_4.5H_2O$)

at 25° C. reduced the conductivity 1.9 percent.; at 40° C. it reduced the conductivity 1.2 percent; and at 55° C. the conductivity was reduced 0.8 percent. The addition of 30 grams of arsenic per liter of the same solution at 20° C. reduced the con-

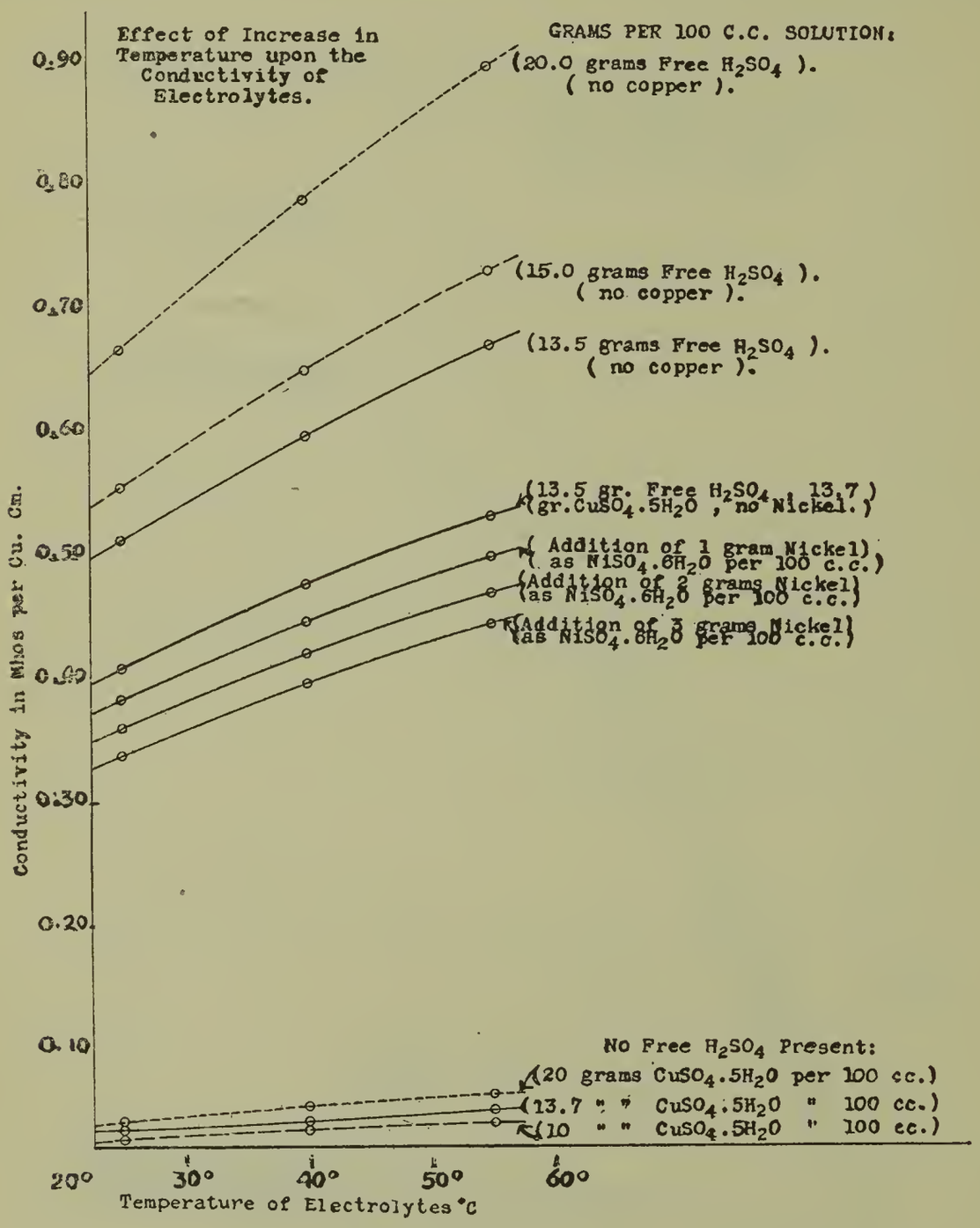


FIG. 7.

ductivity 2.8 percent; at 40° C. the reduction in conductivity was 2.0 percent; and at 55° C. it was 1.4 percent. The addition of 40 grams of arsenic per liter of electrolyte at 20° C. reduced the conductivity 3.6 percent.; at 40° C. the reduction was 3.1 percent; and at 55° C. it was 2.1 percent.

7. The presence of nickel in copper refining electrolytes greatly decreases the conductivity. The addition of 10 grams of nickel as sulphate per liter of an electrolyte containing 135 grams free sulphuric acid and 35 grams copper (137 grams $CuSO_4.5H_2O$) at 25° C. reduced its conductivity 6.5 percent; at 40° C. the reduc-

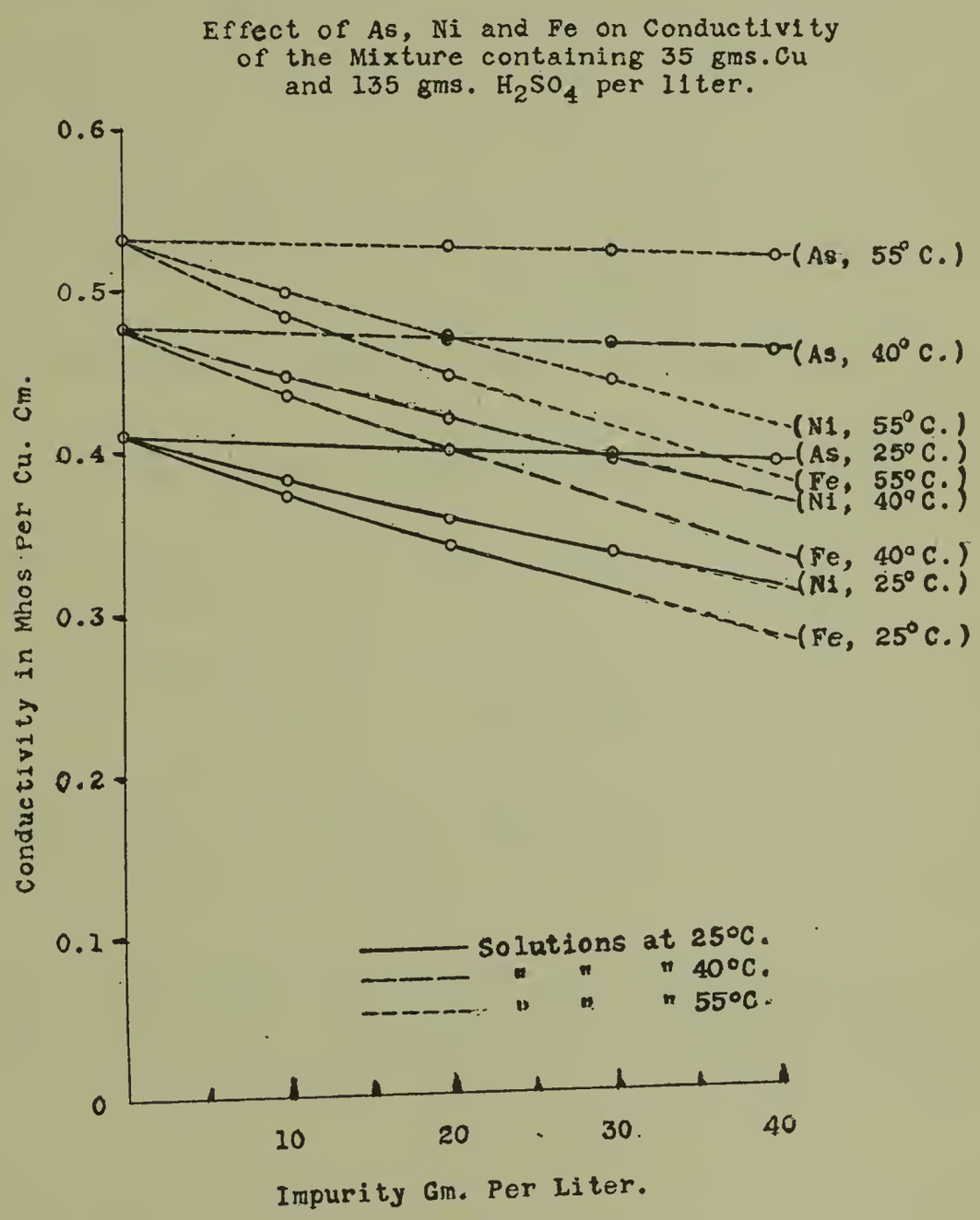


FIG. 8.

tion in conductivity was 6.4 percent; and at 55° C. it was 6.2 percent. When the nickel content was increased to 20 grams per liter of electrolyte the reduction in conductivity at 20° C. was 12.2 percent; at 40° C. it was reduced 11.8 percent; and at 55° C. the reduction was 11.6 percent. When the nickel content was increased to 30 grams per liter of electrolyte the conductivity at

25° C. was reduced 17.5 percent; at 40° C. the reduction was 17 percent; and at 55° C. it was 16.3 percent.

8. The presence of iron as sulphate in copper refining electrolytes greatly depresses the conductivity. The addition of 10 grams of iron as ferrous sulphate per liter of electrolyte containing 135 grams of free sulphuric acid and 35 grams of copper (137 grams $CuSO_4.5H_2O$) at 25° C. reduced its conductivity 8.5 percent; at 40° C. it was reduced 8.8 percent; and at 55° C. the depression was 8.9 percent. When the iron content of this electrolyte was increased to 20 grams per liter the conductivity at 25° C. was depressed 16.4 percent; at 40° C. the depression was 16 percent; and at 55° C. it was 15.8 percent.

9. The conclusions drawn from the results of these determinations are—

(a) The copper content of refining electrolytes should be kept between 30 and 35 grams per liter (approximately 120 to 140 grams $CuSO_4.5H_2O$) and the free sulphuric acid as high as economy permits up to 175 grams per liter. With higher free sulphuric acid content the solubility of copper sulphate decreases rapidly, and also, the added increase in conductivity with more concentrated sulphuric acid is relatively not so rapid.

(b) Maintain the temperature of the electrolyte as high as economy permits. The economical temperature limit seems to be 55° C.

(c) Keep nickel and iron content of the electrolyte as low as possible, as the presence of sulphates of these metals greatly depresses the conductivity of the electrolyte.

DISCUSSION.

Lawrence Addicks[1]: Adsorption at the electrodes is the real key to the practical application of these results and for this reason we should be a little cautious about accepting the conclusion that on account of certain specific resistances we should carry a certain percentage of acid and certain impurities, because we may get

[1] Consulting Engineer, New York City.

totally different practical results in the cell due to the large relative adsorption factor. I hope that Dr. Kern will have an opportunity later to investigate how variations in composition affect the adsorption.

WM. BLUM[2]: There are two closely related points in this paper that I thought might prove of interest. First, I am going to make a plea in this and other connections, in the study of the properties of solutions, for the fixing of the concentrations in definite and comparable units. I will put it this way; we may state that practically the man in the copper refining industry is interested in the amount of copper and the amount of acid in the electrolytes. We will not differ on that at all, but simply to state that he could find that out just as easily if the solutions were expressed in terms of equivalents; or in other words, of normalities, so that a simple picture would be shown of the comparative effect of these various substances on the properties, in this case the conductivity of the electrolyte. I do not recall the exact figures, but in this paper we have given the effect of the conductivity of nickel sulphate; that is, the effect of nickel sulphate and iron sulphate upon the conductivity of copper sulphate solutions containing sulphuric acid. The concentrations are given in absolute amounts and not in equivalent quantities, and therefore it is not easy to compare the effects of these different constituents without having to translate them into exact normalities. The second point is that a casual inspection of the data indicates a very interesting, not a new but sometimes overlooked fact, and that is that the addition of any sulphate to a solution containing a large amount of free acid, such as this copper sulphate bath, makes a large and very nearly equivalent effect upon the conductivity. In other words, it does not make much difference if you add a certain amount of copper sulphate or nickel sulphate or iron sulphate to your bath containing a large amount of free acid, you will produce nearly equivalent changes in the conductivity of the bath. That, I say, has been pointed out in a paper a few months ago upon the conductivity of zinc electrolytes, in which it was shown that the addition of magnesium sulphate to a zinc sulphate solution containing free sulphuric acid decreased the conductivity of the bath. Now I simply

[2] Chemist, Bureau of Standards, Washington, D. C.

suggest that if these data had been plotted in terms of normalities, these facts would have been brought out more clearly and perhaps more usefully.

M. R. THOMPSON[3] (*Communicated*): Dr. Blum has pointed out that the depression of conductivity of the electrolyte due to the addition of nickel, iron, etc., is only about the same as would be obtained by increasing the copper content by an equivalent amount; in other words, it is simply another aspect of the "common ion" effect. Conclusion 9 (c) in the summary might therefore just as well read: "It is just as important to keep the copper content of the electrolyte down to the minimum figure for satisfactory operation, as it is to keep the nickel and iron content as low as possible, since the presence of *any* metal sulphate greatly depresses the conductivity of the electrolyte."

It is interesting to secure some results for comparison, by interpolation. Thus, in an electrolyte containing 35 grams of copper and 135 grams free sulphuric acid per liter, at 40° C., increasing the nickel content from 0 to 30 grams per liter decreased the conductivity by 17 percent (p. 196). From the curves of Fig. 5, we find that, in a sulphuric acid solution of a strength of 15 grams per 100 cc., at 40° C., increasing the copper content from 0 to 30 grams per liter (0 to 11.8 grams $CuSO_4 . 5H_2O$ per 100 cc.), decreases the conductivity of the solution by about 17 percent. Similarly, for a solution of 10 grams per 100 cc. of sulphuric acid, at 40° C., the reduction would be about 19 percent. This is about the same effect as that of the addition of a nearly equivalent amount of nickel to the typical copper sulphate and sulphuric acid electrolyte. Iron, however, is not quite so important as nickel in depressing conductivity. The very slight effect of arsenic upon the conductivity suggests that it is present in an undissociated compound.

EDWARD F. KERN (*Communicated*): Adsorption, which in the case of electrolysis is the tendency of a film of gas to condense upon the surfaces of the electrodes and to adhere tenaciously, is no doubt one of the causes which consumes some of the power required for the electrolytic refining of metals, but I think that it is not the real key to the practical application of conductivity

[3] Bureau of Standards, Washington, D. C.

results, any more than concentration-polarization is. The major part of the potential drop between the anodes and cathodes (when arranged according to the multiple or parallel system) in a properly circulating copper refining electrolyte, and not including the potential drop due to metallic and contact resistances, is the result of the resistance of the electrolyte, which is approximately 80 percent of the total potential drop, whereas that which is due to adsorption and to concentration-polarization, is between 11 and 14 percent, and that due to the coating of non-conducting anode residues is from 9 to 6 percent. The most readily controllable resistance in a copper refining cell is that of the electrolyte, which is accomplished by varying the free sulphuric acid content and by heating, whereas the resistance due to adsorption and to the coating of anode residues seems to be a function of the character of the electrodes and to the impurity of the anodes. In the case of concentration-polarization, it increases with increase in current density, with lowering of the temperature, and with decrease in the rate of circulation. So, having selected an electrolyte which possesses the highest economical specific conductivity, the further means of reducing the power consumption seems to be by carrying the pyro-refining of the metal to the highest degree and poling the refined metal to as high pitch as economically possible before casting the anodes, thus producing anodes having dense smooth surfaces and low in impurities. I doubt if any variation in the concentration of either sulphuric acid or of copper sulphate, within the limits of that of commercial copper refining electrolytes, will have any decided effect upon the resistance due to adsorption, because the phenomenon of adsorption has to do only with the saturated surface film of gas of a thickness of one molecule of the adsorbed gas. So it seems that, after all, the only practical means of reducing the power consumption in an electrolytic refining tank, in which are anodes containing a definite amount of impurities and having definite physical character, would be by selecting an electrolyte which has the highest economical specific conductivity, and to operate it at as high temperature as conditions permit.

The minimum copper sulphate content of the electrolyte is controlled by the current density at which the refining is conducted; the higher the current density the higher must be the copper sulphate content, and the lower the current density the lower should

be the copper sulphate content. As the current density determines the minimum copper sulphate, then the free sulphuric content of the electrolyte is the important factor which controls the power consumption in the cell, or tank. If the copper sulphate content is too low, the cathode deposit will form unsatisfactorily due to simultaneous liberation of hydrogen with the copper. There is reason to believe that the resistance of the adsorbed films on the electrodes is a fixed quantity for electrodes of definite physical character and for anodes containing a definite percentage and kind of impurities. Apparently the means for readily reducing the potential drop in the refining tank is to select the most economical free sulphuric acid concentration, keep the metal sulphates (copper, nickel, etc.) as low as possible, heat the electrolyte between 55 and 60° C. (130 and 140° F.), and maintain its circulation at such a rate as not to cause excessive loss of anode residues nor contamination of cathodes by mechanical occlusion of anode residues. The revised conclusion, 9 (c), as suggested by Mr. Thompson, is very acceptable.

Following the suggestion made by Dr. Blum that the results would prove more interesting if they had been given as normality or gram-equivalent concentrations instead of grams per 100 cc.; it so happens that 5.0 grams free sulphuric acid per 100 cc. solution is approximately a normal solution, 10.0 grams per 100 cc. = 2 *N.*, 13.5 grams per 100 cc. = 2.7 *N.*, 15.0 grams per 100 cc. = 3 *N.*, and 20.0 grams per 100 cc. = 4 *N.* In the case of $CuSO_4 . 5H_2O$ concentrations, 5.0 grams per 100 cc. = 0.4 *N.*, 10.0 grams per 100 cc. = 0.8 *N.*, 13.7 grams per 100 cc. = 1.09 *N.*, 15.0 grams per 100 cc. = 1.2 *N.*, and 20.0 grams per 100 cc. = 1.6 *N.* One gram nickel per 100 cc. = 0.3 *N.*, 2 grams nickel per 100 cc. = 0.6 *N.*, and 3 grams nickel per 100 cc. = 0.9 *N* These figures will permit of obtaining the results in terms of gram-equivalent or normality concentrations by applying them to the several figures. I am sorry that these figures were not made a part of the curves.

The discussions have suggested several lines of investigations, which I hope to get under way within a short time.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 28, 1922, President Acheson Smith in the Chair.

CORROSION BY ELECTROLYTE CONCENTRATION CELLS.[1]

By Robert J. McKay[2]

Abstract.

Calculations of the E. M. F. generated on metal electrodes of the same metal by different concentrations of copper sulphate are given. Also, the results of determinations showing greatly accelerated corrosions of homogeneous metal in acid solution, due to differences in concentration of dissolved materials in the solution.

In a recent study of the rate of corrosion of acid-resisting metals in acid solutions, a type of electrolytic corrosion which is ordinarily neglected in considering corrosion in general was shown to be of importance. This action is that of electrolytic cells which corrode metal in certain anodic areas, the position of these areas and the electromotive force of the cell being governed by differences in the concentrations of the substances dissolved in the corroding solution. Such a cell is distinct from the type ordinarily considered, which is generated by differences in the corroded metal. It is believed that, while the particular corrosion studied is of rather limited and local interest, the possibilities of the explanation and remedy of various instances of corrosion according to analogous reasoning is great enough to justify the present paper.

In the corrosion of acid-resisting metals by the acid solutions used in pickling steel sheets, a small amount of copper from the metals may go into solution. Under certain conditions it is found that variations in the amount of copper in solution would produce an E.M.F. as high as 0.2 volt. This voltage in the highly

[1] Manuscript received February 28, 1922.

[2] Industrial Fellow of the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

conducting acid solution will produce rates of corrosion up to 50 times the normal rate, thus, under the worst conditions, reducing the service of a piece of apparatus from a period of years to as many weeks. This extreme condition is not usually reached in practice, but it is approached nearly enough that the corrosion of these cells is an extremely serious matter to the steel pickler.

In addition to this particular type of cell it has been demonstrated that economically important corrosion may be produced by cells due to differences in the concentration of acids, concentration of dissolved oxygen or hydrogen, or concentration of dissolved oxidizing and reducing salts, for example the presence of ferric iron at one point and of ferrous iron at another. These cells may, therefore, be quite widely distributed.

The single potential of a copper electrode in normal $CuSO_4$ solution is +0.392 volt, referred to the normal hydrogen electrode as zero.[3] It is thus the most noble, that is the most easily replaced from its solution, of all the common metals. This fact makes it an experimentally valuable and logically important example for use in the study of such electrolyte concentration cells.

In practice these cells are usually set up by differences in the rate of movement of the corroding solution, or, more effectively, by movement of one part of the solution while another part remains practically stationary. In this way, for instance, one part of a solution may be aerated while another is protected from the action of air, and thus an oxygen cell or an oxidizing and reducing salt cell is set up. Or the stagnant portion may become more and more saturated with the products of corrosion, while the moving portion sweeps them away leaving solution low in concentration of corrosion products.

In the particular case studied copper is dissolved from the tie rods of pickling tanks, the acid-resisting alloy of which these rods are made usually containing copper. The rods are imbedded in the wood of the tank throughout practically their entire length, but may be in contact at certain points with the main bath of pickling acid. They are always wet with the acid, but along most of their length this moves slowly, if at all, and gradually becomes more and more concentrated in copper salts. The tank acid is practically free from copper at all times, both because there is no source

[3] Lewis, System of Physical Chemistry, Page 204.

of supply and because in the pickling reaction copper, if present, is precipitated. Therefore at the points of contact with the main bath the rods are in contact with a solution containing very little copper, and thus an electrolytic cell is set up with the anode at the point of contact with the bath, and the metal is rapidly corroded at that point.

To calculate the probable E.M.F. of such a cell let us consider the simplest case chemically, that is an apparatus of copper in contact with an acid solution which moves at one place and is stagnant at others. There is always a slight attack of the metal, and therefore the solution which is stagnant immediately becomes more concentrated in copper at the surface of the metal than that which is moving. We thus have two copper electrodes connected in external circuit, and in contact with solutions of two different copper concentrations. According to Nernst, the E.M.F. of each electrode of such a cell may be calculated by equating the electrical work done when a small quantity of the metal from the electrode goes into solution or out of solution, to the mechanical work due to its change in volume and pressure.[4] By this method the following formula for the voltage of such a cell is derived, neglecting the small potential at the junction of the two solutions.

$$E = \frac{RT}{nF} \ln \frac{C}{c}$$

Wherein E is the electromotive force of the cell in volts,
R is the gas constant in joules per degree,
T is the absolute temperature,
n is the valence of the metal,
F is the Faraday, 96500 coulombs,
C is the ionic concentration of the metal in the more concentrated solution,
c is the ionic concentration of the metal in the less concentrated solution.

For practical use this formula may be evaluated replacing natural logarithms by logarithms of the base ten, and assuming a temperature of 18° C., at which point measurements of the conductivities of various concentrations of copper sulphate are available.[5] Thus evaluated the formula becomes

$$E = 0.0289 \log \frac{C}{c}$$

[4] Lewis, A system of Physical Chemistry, Vol. 2.
[5] See Landolt-Bornstein-Roth Tabellen.

For comparison with practical pickling conditions the temperature must be considerably higher than this, probably 82° C., and the formula for this temperature becomes

$$E = 0.0352 \log \frac{C}{c}$$

The ionic concentrations, C and c, at 18 degrees may still be used in this formula, since they vary slightly with the temperature themselves, and therefore the ratio of one to the other which is of importance in the formula will vary even less.

The conditions of practice are that at one electrode the concentration of copper approaches nearly to zero, and these conditions were approximately duplicated in the experiments. The above formula will not give finite values for a concentration of zero, and neither can this condition be actually reached in practice or in the laboratory. The concentration at which copper become determinable electrolytically in the solution has therefore been selected as approximately the smallest concentration which is practically attained. This is in the neighborhood of 0.0001 *N* or about three milligrams of copper per liter. Calculations follow of the voltages of cells made up of two copper electrodes, one immersed in 0.0001 *N* copper sulphate and the other in a more concentrated solution. For the ion concentration ratio the ratio of the product of the equivalent conductances at the various dilutions by the concentration are used. For instance, for the cell

$$Cu : 0.001CuSO_4 :: 0.0001CuSO_4 : Cu$$
$$E = 0.0352 \log (0.0985/0.0110) = 0.033$$

The following table shows the values obtained for the range of cells studied:

Anode Concentration	Cathode Concentration	E. M. F.
0.0001 *N.*	0.001 *N.* (0.032 g/L.)	0.033 volt
0.0001 *N.*	0.01 *N.* (0.32 g/L.)	0.064 volt
0.0001 *N.*	0.1 *N.* (3.2 g/L.)	0.092 volt
0.0001 *N.*	1.0 *N.* (32 g/L.)	0.13 volt

If the electrode is an alloy of copper with some other metals, as in the case of most of the acid-resisting metals, there is, besides

the above calculated E.M.F., an additional force. For instance, consider monel metal, which was the principal alloy studied. When the electrolyte concentration cell acts on monel metal, instead of the solution of one equivalent weight of copper at the anode, the solution of an equivalent of metal 70 percent of which is nickel and 30 percent copper takes place. The energy change here is the energy of the reaction,

$$0.7Ni + 0.3Cu + CuSO_4 = 0.7NiSO_4 + 0.3CuSO_4 + Cu,$$

and the additional voltage of the cell might be expected to be that generated by such a reaction. This, according to the values of the single potentials of copper and nickel in normal solutions of their salts would be 0.39 volt. But the matter is complicated by the fact that we are dealing with a solid solution, and the energy changes when the above reaction takes place with monel metal as the source of the metallic nickel and copper are different from those when the metals are dissolved in each other. The voltage due to the solution pressure of the metal is thus lessened, being apparently only about 0.05 volt instead of the value mentioned above, which should exist in the presence of pure nickel. This figure added to the calculated results given above would make them approximately agree with those determined experimentally as is shown by the curve, Fig. 1.

The whole practical value of these determinations lies in the light which they throw on possible changes in the rate of corrosion under the conditions indicated. The rate of corrosion besides depending on the voltage developed is affected also by conditions such as the resistance of the circuit, the oxygen content of the solution, and the numerous other things which affect anode corrosion. Therefore a number of experiments were made in which the loss of weight of the corroded anodic area was determined under varying conditions as well as the voltage developed. The experimental difficulty of such determinations is large, and up to the present time only sufficient work has been done to map out the field in a manner sufficiently accurate to indicate the importance of several variables. Some results are given below of experiments in which the concentration of copper sulphate at the

cathode was varied while the anode was always in pure sulphuric acid (60 g./L. or 8 oz./gal.) at the beginning of the experiment.

The greatest difficulties in these experiments are the making of a low-resistance connection which is easily removed without danger of affecting the weight or electrical properties of the anode, and the control of the concentration changes which must necessarily take place during an experiment of sufficient length to obtain a measurable loss in weight of the anode. These diffi-

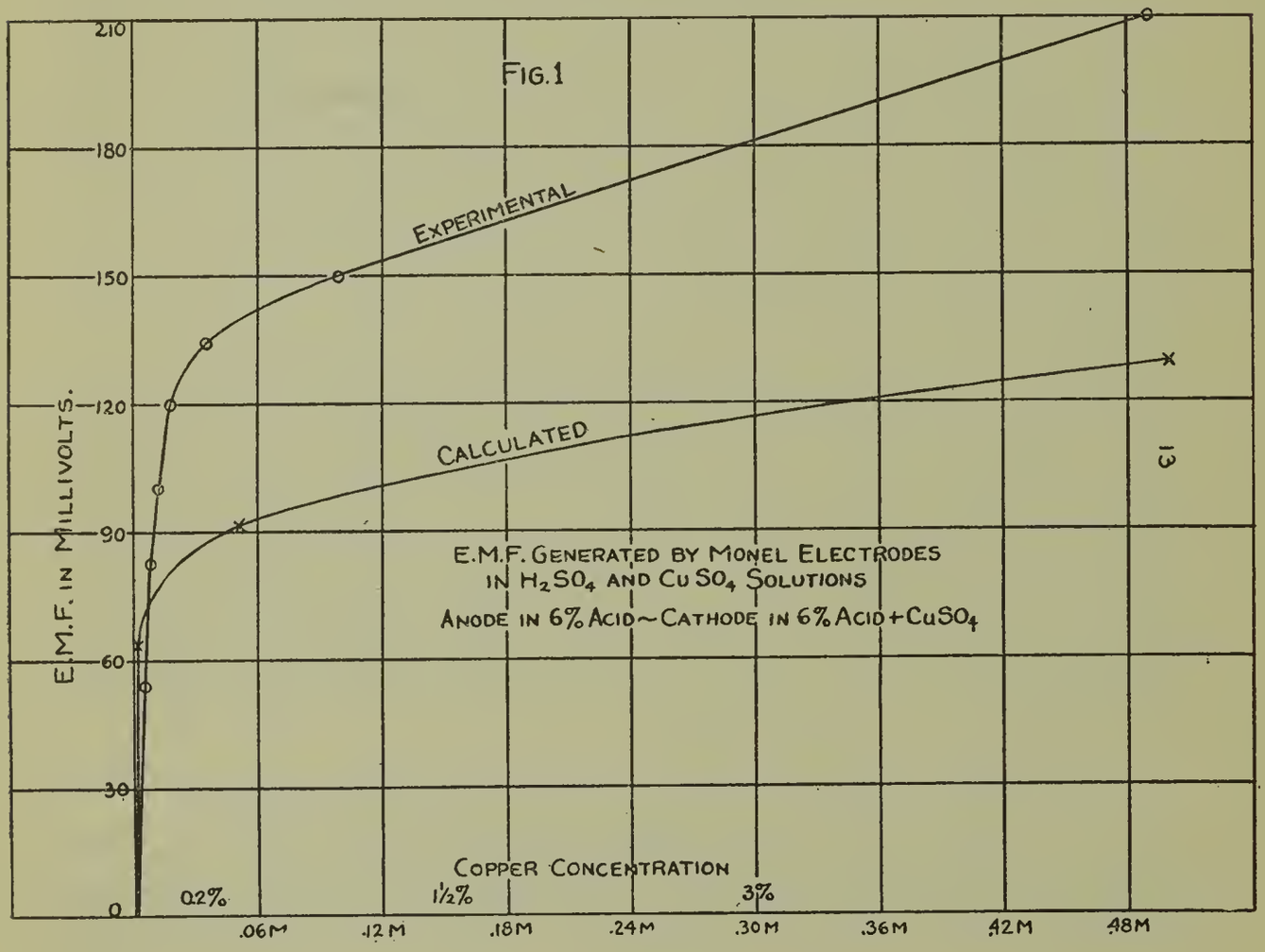


FIG. 1

culties are not at all insurmountable, but in the present experiments it was considered better to sacrifice some accuracy in order to cover the interesting ground, and, therefore, errors due to them are undoubtedly present. The drop in voltage due to concentration changes during an experiment was usually between 25 and 50 percent of the total voltage. The magnitude of the current developed in the apparatus was in the neighborhood of 0.03 ampere. Details are shown in Table I. The concentrations given are those at the beginning of the experiment, and the

voltages are an average of several readings during the corrosion. It is seen that the corrosion rate when there is a high concentration of copper at the cathode is over 40 times that shown in the first test with zero concentration at the cathode.

TABLE I.

Data of Corrosion Tests

Temperature °C	Concentration Molar	E. M. F. Volts	Corrosion Rate Mg./dm.²/day
82	0.0	0.0	150
90	0.003	0.12	1700
*84	0.003	0.12	*1426
85	0.005	0.12	2260
?	0.03	0.10	3108
85	0.03	0.12	4830
78	0.2	0.14	6374
78	0.3	0.15	6236

*In this test resistance was placed in the circuit increasing the natural resistance of the cell itself, 9 ohms. A corrosion of 150 milligrams per square decimeter per day would produce 3 mm. penetration in about 6 years while 6374 milligrams per square decimeter per day would produce the same penetration in about 7 weeks.

In some tests comparing electrodes of different metals, other acid-resisting metals were found to be more rapidly corroded by electrolyte concentration cells than monel metal. For instance, with a pure aluminum bronze of about 9 percent aluminum the rates of corrosion were:

Monel Metal .....4030 mg/dm²/day
Aluminum Bronze .....7490 mg/dm²/day

In addition to electrolyte concentration cells of the above type it was demonstrated that other forms of cells exist whose E. M. F. is due to the corroding solution instead of the metal. With one electrode in acid saturated with hydrogen, and one in acid saturated with oxygen, a millivoltmeter reading of 0.026 volt was obtained. By the use of different concentrations of sulphuric acid at the electrodes a galvanometer throw was produced. The E. M. F. generated in this case is quite small except when the acid concentrations are so minute that the ratio between concentrations may be large. With the presence of ferrous sulphate at one electrode and ferric sulphate at the other, the E. M. F. read-

ings were of approximately the same order of magnitude as in the copper sulphate cells. The electrode surrounded by ferrous sulphate is the anode.

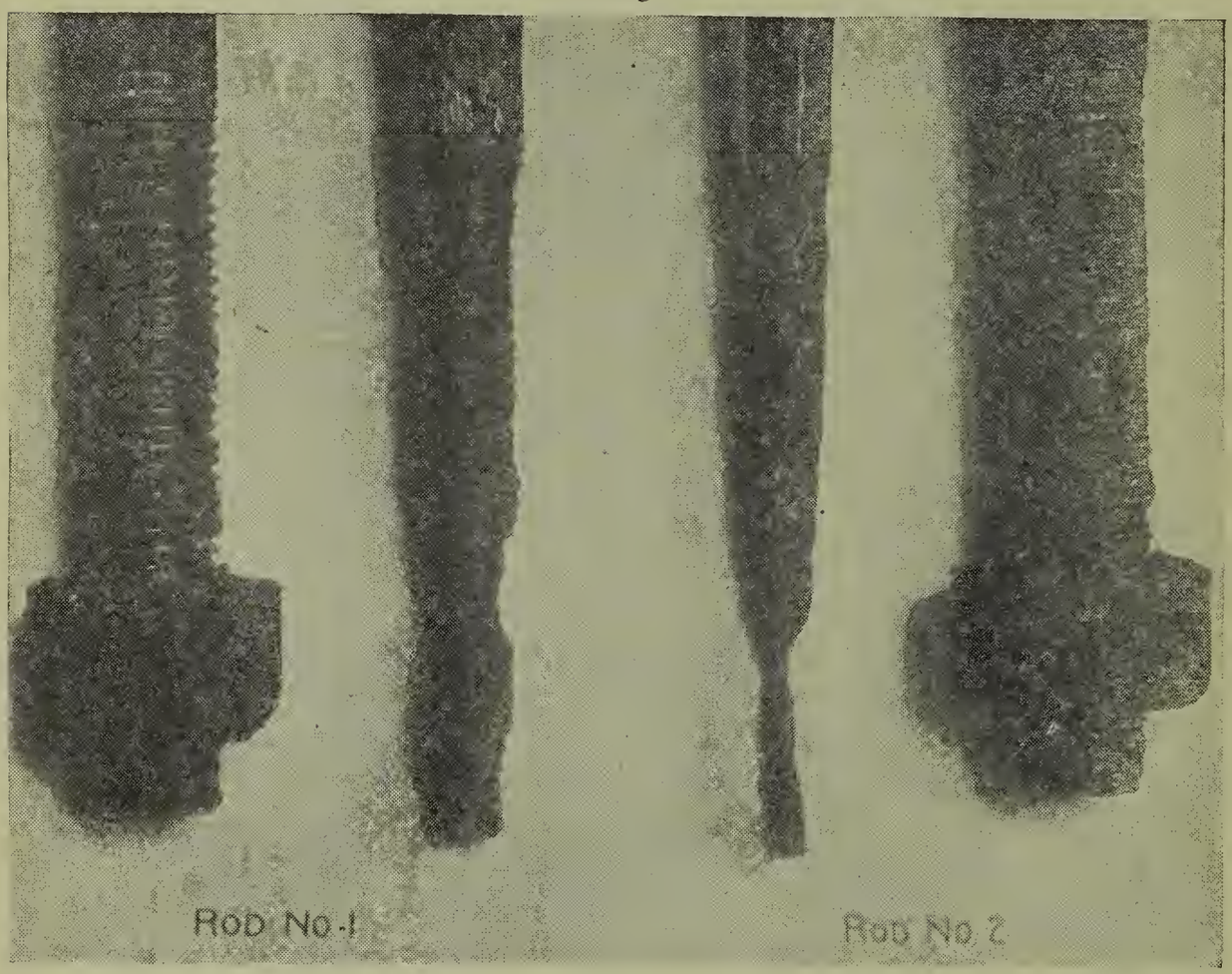


Fig. 2.

Fig. 3.

In general an electromotive force can be produced in any case where corrosion is taking place, by more violent agitation of the corroding solution around one electrode than the other. The existence of this condition follows directly from the fact that the corrosion reaction must produce concentration differences in the

reacting materials in the film in contact with the metal. This was checked in the case of the copper sulphate cells by the following experiment:

A cell was set up with monel metal electrodes in sulphuric acid (60 g./L. or 8 oz./gal.), the solutions around the two electrodes being separated by a porous cup. The electrodes were connected in external circuit through a galvanometer. When the solution around one electrode was stirred and the other allowed to remain quiet, a deflection of the galvanometer was obtained showing a flow of current through the cell, the agitated electrode being the anode. The current continued as long as the stirring was kept up. If the solution at the other electrode was now stirred and that first stirred allowed to come to rest, the current was reversed. It was also found possible to produce a current with both solutions agitated, by making the agitation at one electrode more violent than at the other. The direction of the current was always such that the more violently agitated electrode was the anode.

In pickling steel, this form of corrosion causes the final discarding of nine out of ten of the tie-rods used to bolt together the tanks for holding acid. These rods invariably show the presence of areas which are much more rapidly corroded than like areas in close proximity. The origin of this condition was for a long time the more mysterious, since the position of the corroded portions was often intermediate between complete exposure to the wash of fresh acid and the partial protection from acid obtained by embedding in the wood. But this is just the point at which the action of these cells takes place, since the flow of current from the rod will be at the nearest point to the cathodic area, at which a reasonably low concentration of copper sulphate exists.

It is common to see tie rods which come from a leaky tank deeply marked by corrosion at each joint between timbers, and to find places where a tie rod one inch in diameter is almost completely corroded through, and a few inches from this point is practically of the original size. Figures 2 and 3 are photographs of rods which have been affected by electrolyte concentration cell corrosion.

Figure 4 is a diagrammatic representation of the way these cells act between two timbers of a tank. The cure of this condition is a question of correct construction in each case, the general rule being that acid should not be allowed to lie quiet for long periods in contact with metal which is also exposed to fresh acid. In the above case it has been suggested that the holes for the rods be drilled somewhat larger and connected with the tank by cross drilling.

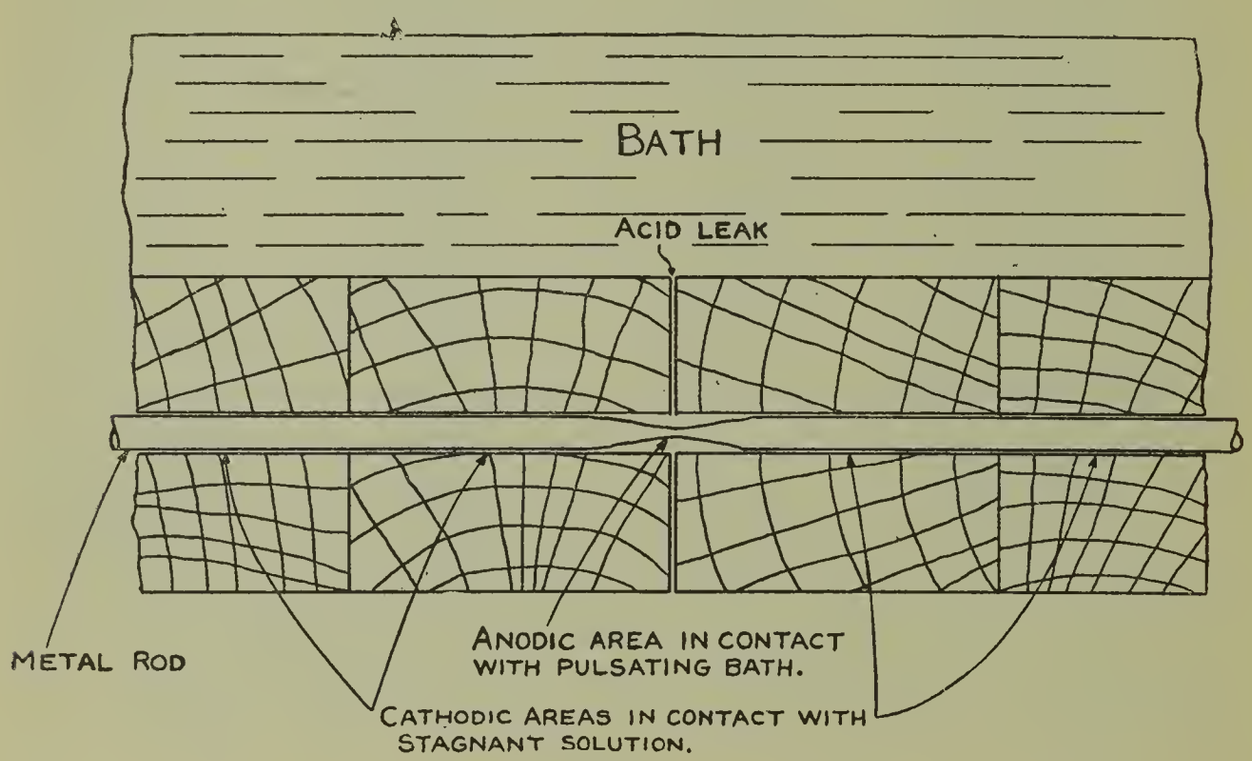


FIG. 4.

It may be of interest to mention another factor of importance which was noted in the course of these experiments. This is the effect on the rate of any corrosion of the dissolved air content of the solution. It is sometimes the tendency in the study of acid corrosion to neglect the presence or absence of air as unimportant compared to the concentration of a strong acid such as sulphuric. But it was found in the present experiments that the normal rate of corrosion of monel metal in air-free sulphuric acid at 82° C. (60 g./L. or 8 oz./gal.), 135 to 150 mg/dm^2/day, was increased to about 700 mg/dm^2/day in solution saturated with air. The corrosion of other acid-resisting metals was increased in proportion. This means that the conditions of air saturation must be known in all cases if the results of corrosion experiments

are to be applied to practice. The agitation or non-agitation of samples is another matter of importance, since this determines the relative concentrations of chemicals in the film of solution in contact with the metal. This is particularly of importance when oxygen aids in the corrosion, because the low possible maximum concentration of the dissolved gas in equilibrium with the atmosphere changes rapidly as the corrosion proceeds.

DISCUSSION.

W. C. Moore[1]: This paper recalls some of the discussion we had at Atlantic City last year on corrosion. You may remember that in the discussion of one paper, one of the men pointed out that he had stirred by means of air the solution in which he was trying to determine the relative degree to which pure iron and iron with copper in it were corroded. The point that Mr. McKay has just brought out, occurred to me at that time, that by stirring with air you will very probably increase the rate of corrosion and, so far as I know, no one had then studied that or pointed it out from an experimental standpoint. It is very interesting to know that Mr. McKay has substantiated my statement.

Colin G. Fink[2]: Mr. McKay, on page 209, says: "A cell was set up with monel metal electrodes in sulphuric acid (60 g./L. or 8 oz./gal.), the solutions around the two electrodes being separated by a porous cup. The electrodes were connected in external circuit through a galvanometer. When the solution around one electrode was stirred and the other allowed to remain quiet, a deflection of the galvanometer was obtained showing a flow of current through the cell, the agitated electrode being the anode. The current continued as long as the stirring was kept up. If the solution at the other electrode was now stirred and that first stirred allowed to come to rest, the current was reversed." This brings up a very important point, a point that was discussed last Monday at the meeting of the National Research Council Corrosion Committee, namely, that it is highly important that we come to some definite understanding as to what is the proper method of deter-

[1] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.
[2] Consulting Electrometallurgist, New York City.

mining corrosion losses. You can readily see that two investigators might set up a piece of apparatus with the purpose of determining the corrosion of an alloy or a metal and each investigator carry out his results very carefully, and yet the results of one be entirely opposite to those of the other, depending, as is indicated here very strikingly, whether the solution around the one sample was stirred and in the other case was not. We have unfortunately been confronted with statements made by a number of investigators who have studied the resistance to corrosion of certain alloys; these investigators have found that by suspending alloy samples in a quiet solution, that there was practically no loss in weight. They therefore draw various conclusions; among others, for example, they suggest that this alloy is a good alloy to be used in acid pumps, since it will withstand the acids which are carried by these pumps. Now as soon as a pump manufacturer gets a sample of this alloy and makes a bearing or other internal part of a pump out of this alloy, he finds that the alloy goes to pieces very fast, even when pump solutions are absolutely free from gritty material. As brought out by Mr. McKay, it is absolutely essential that we take into account the concentration of the electrolytes directly at the metal. I hope that within another year the corrosion committee will have something definite to suggest. The suggestions will be forwarded to our Society and our Society given an opportunity to discuss them and vote upon them.

C. J. Thatcher[3]: In 1903, while in Leipsic studying electrode processes with platinized electrodes, I found that although the electrodes had been standing in the electrolytes, sometimes as much as a day, as soon as I began to stir there would be either an increase or decrease in the potential. But I also found that I got a different effect according to whether I had nitrogen or oxygen over the electrolytes.

It finally developed that the effect of the stirring was not due to changes in concentration of the electrolyte, but to the rate at which dissolved oxygen was brought to the electrodes by the stirring. I proved that by adding a catalytic agent to the electrolyte, which retarded or inhibited the oxidizing action due to dissolved oxygen. When I added what I called a "poison" at that time, *e. g.*, mercuric cyanide, to an electrolyte, when I stirred

[3] New York City.

the solution there was no change in the potential in either an oxygen or nitrogen atmosphere.

I think Mr. McKay might find a similar test interesting. It should be interesting to find out whether the variations in potential are due to concentration changes or to the rate at which oxygen is brought to the surface of the electrode—both of which can be produced by stirring, of course.

A. L. FEILD[4]: According to the ordinary definition, the term "concentration cell" refers to a cell in which two copper electrodes, for instance, are immersed in two solutions of a copper salt of different concentrations. When the circuit is completed, copper dissolves from the electrode in the solution of lower concentration and is deposited on the electrode in the more concentrated solution. If this were the usual type of electrolytic process operating in progressive corrosion, the metal undergoing corrosion would dissolve from one surface and be re-deposited on another. As a matter of fact, such is seldom, if ever, the case. For this reason the title of Mr. McKay's paper is misleading.

To any one engaged in corrosion investigations, I would strongly recommend the careful study of the recent work of O. Bauer and his associates (*cf.* Mitt. Kgl. Materialprufungsamt, 1918, **36**, 114-208, Z. Metallkünde, 1919, **10**, 124-204, abstracted in C. A., **13**, 2187; **14**, 261).

In the ordinary corrosion of iron we are dealing largely with the electromotive forces set up by partial pressures of oxygen which are different over areas of the piece undergoing corrosion. We have a system of oxygen-hydrogen cells. Corrosion is due to the liberation of nascent oxygen at the anodes of such cells. The effective oxygen pressure at any particular point is determined (a) by the availability of gaseous or dissolved oxygen, (b) by the degree to which the iron surface at this point is able to function as an oxygen carrier, and (c) by the hydroxyl (or hydrogen) ion concentration.

ROBERT J. MCKAY: The effect of oxygen on this corrosion is interesting. It is a matter of common knowledge, and was brought out a year ago at our Society meeting how effective oxygen is, in general, in producing corrosion; but oxygen, I think, has been

[4] Carbide and Carbon Res. Lab., Inc., Long Island City, N. Y.

neglected in the study of corrosion in acids. Dr. Fink's suggestion about stirring is much to the point. I found that reproducible results were obtained only when the solution was uniformly stirred. This is probably due to surface adsorption, and surface films which may be or may not be protective. The errors in a test which is supposedly quiet are often large. Apparatus for producing perfect quiet in the average laboratory is unusual and slight movements may produce errors of several hundred percent. I believe that corrosion experiments should be carried out on some sort of an agitating apparatus. A mechanical agitation seems better than agitation with gas bubbles because it admits of separate control of dissolved gases and agitation rate.

The point brought out regarding the supply of oxygen to the electrode is a most interesting one; in fact, that is what I consider produces the concentration effect. If the oxygen or the corroding agent, whatever it happens to be, is not furnished to the electrode rapidly enough by stirring, the concentration immediately approaches zero in the film around the electrode and the concentration in the film depends on the rate of supply of the corroding agent to the corroded material.

In regard to the use of the term concentration cells, it is true that the action which occurs is not completely reversible and the cell is therefore not a concentration cell in the present accepted sense. This term is, however, more nearly descriptive of the action than any other which has suggested itself, and was therefore adopted. I would disagree with the statement that the practical corrosion is in a direction which is opposite to the theoretical concentration cell; in fact I have shown in these calculations that in general the trend is in the same direction. Referring to the diagram, the pressure will be for copper ions out of the solution in this case, and into the solution in that. The corrosion will be on this electrode, as calculated according to the theoretical concentration cell.

In regard to the effect of oxygen and hydrogen or other gases in the solution, I made no study of those factors particularly, being more interested in the concentrations of the metal in solution. The reactions which may take place with oxygen and hydrogen were too complicated to go into at that time. However, I used an apparatus which quite effectively prevented differences

or errors due to such concentrations. I used a funnel, as shown, and below it was a saturating apparatus consisting of a glass tube ending in an alundum crucible and this tube was connected to a supply of some gas which seemed the best to have in the solution, while the measurements were being made. Most of the measurements were made in solutions saturated with nitrogen gas, selected as being neutral. Tests were also made with solutions saturated with oxygen gas, with hydrogen and with air. The gas at both electrodes was kept at the same concentration.

G. B. HOGABOOM[5]: Direct agitation, either by mechanical means or by air, does not give the same results as those obtained when the test piece is removed from the solution and exposed to the air for a few seconds and then returned to the corroding bath. If, for example, a 10 percent sulphuric acid solution is used and any copper alloy is taken for the test, a much higher rate of corrosion will be found if the alternate immersion and exposing to the air method is used. There seems to be oxidation of the metal while exposed to the air and the oxide formed is readily soluble in the acid when the specimen is immersed again. This oxidation does not take place as rapidly if the test piece is permitted to remain in the solution and air is blown against it. The alternate immersion and exposure gives what might be termed a "wash" effect, giving rise to accelerated corrosion. It is believed that the results obtained from such a method would be more comparable to what actually takes place on tie rods of pickling tanks than if the metal being tested is left submerged in the corroding solution.

A. L. FEILD: I think that Mr. McKay has misunderstood my remarks. I simply attempted to point out the fact that the corrosion phenomena which are the subject of his paper cannot be classified as belonging to that type of corrosion which takes place in a "concentration cell" as the term is ordinarily defined.

[5] Research Electroplater, Scovill Mfg. Co., Waterbury, Conn.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 28, 1922, President Acheson Smith in the Chair.

A STUDY OF EFFECT OF IMPURITIES ON STORAGE BATTERIES.[1]

By Helen C. Gillette[2]

Abstract.

The presence of certain amounts of impurities in the electrolyte of a storage cell has been studied to ascertain the effect on the electrical performance of the cell. The extent of the injury has been determined by comparison of the electrical characteristics of the cells before and after contamination and by further comparison with normal cells included in the same series of tests.

Of the metals tested only manganese and platinum produced intense injury when present in minute quantities. With these two exceptions, none of the impurities tested had a lasting effect on the cell voltages or on the ampere hour capacity of the charged battery. In various amounts certain of the impurities were found to be injurious, either by increasing the rate of self-discharge or decreasing the life of the plates. Zinc, nickel and tin in the percentages tested were not detrimental to any of the electrical characteristics. The results of these tests indicate that contrary to the general belief, most of the common metals and acids may be present in appreciable quantities without causing serious injury to the cell.

The increasing use of storage batteries for starting and lighting of automobiles augments the importance of knowing more of both the theoretical and practical functioning of the cell. Among other factors, the necessary purity of materials to insure capacity is of prime importance to the manufacturer. Also the introduction of foreign materials in the adjustment of electrolyte during the service of the cell is not an impossibility. The magnitude of the

[1] A portion of data incorporated in thesis for M. S. degree at Purdue University, Manuscript received February 16, 1922.

[2] Research Laboratory of the Prest-O-Lite Co., Inc.

effect of such introduction has been a source of annoying doubt, although experience abetted by theory has compiled a generous number of proverbs as to the harmful effect of traces of "impurities."

The literature contains frequent references to the injurious effect of foreign materials, but specific data are lacking. The acids, nitric, hydrochloric and acetic attack the structure of the plate, but the concentrations at which these acids are harmful have not, I believe, been previously published. Of the metals, the most concrete reference is in "Accumulators," Dolzalek, in which it is stated that those metals existing in more than one valence and which are above lead in the electromotive series cause an abnormal loss of capacity on standing. Those metals which are below lead plate out on the negative electrode, resulting in local action and the rapid discharge of that plate. Vicarey[3] has done considerable work on the detrimental effects of ammonia, and advises the manufacture of storage batteries at points as far distant from human habitation as possible, to eliminate this deleterious gas. With the present-day experience in the frequent use of ammonium salts in plate manufacture, the conclusions of Vicarey are of amusing historical interest.

In interpreting data upon storage cells it must be remembered that lead cells cling tenaciously to individual rights of performance. This is especially true with reference to capacity and rate of self-discharge. Therefore, in order to distinguish the effect of the added impurity with greater certainty from the idiosyncrasies of the individual cells, the latter were put through preliminary cycles of charge and discharge until the ampere hour output had attained a constant and characteristic value. This established the history of the cells prior to their employment in the test and prevented the use of abnormal cells. The standardization of each test cell was the more important because it was impracticable to allot more than two cells to each combination owing to the number of combinations studied. In spite of the limited number of cells the observations are therefore considered substantially indicative, but are not presented as quantitatively final in every case.

[3] Trans. Faraday Society, 1905, **1**, 271; 1906, **2**, 222.

In each series two uncontaminated cells were included, making eighteen cells in all, from which the average capacity and life of the entire group of batteries could be very reliably determined. The metallic impurities used were antimony, arsenic, cadmium, iron, magnesium, manganese, mercury, nickel, platinum, tin, silver, and zinc. These were introduced as solutions of their salts. The contaminating acids employed were acetic, hydrochloric and nitric. The impurities were in all cases added in definite percentages of the electrolyte by weight.

The characteristics of storage battery performance which might be adversely affected are classified under four headings:

1. The ampere hour capacity or output of the battery on discharge.
2. The voltage characteristics on charge and discharge.
3. The rate of self-discharge of the charged battery upon standing.
4. The life of the active material, which is conditioned mainly by the rate of mechanical disintegration in successive cycles.

Experimentally, the changes in these characteristics were determined by measurements of (1) the ampere hour capacity on discharge immediately following charge; (2) voltage characteristics on charge and discharge; (3) loss of capacity on standing for definite time intervals after charge; and (4) the relative life compared with uncontaminated cells.

EXPERIMENTAL OBSERVATIONS.

The effect of the impurities on the ampere hour output of the charged battery was surprising. It had been anticipated that the impurities, especially those metals readily capable of oxidation, would produce considerable change in the capacity of the cells. However, contrary to this expectation, the tests showed that the discharge capacity was unaffected except in three cases, namely, silver, manganese and platinum, which will be considered in more detail later.

Likewise, observations of the voltage characteristics showed them to be unexpectedly impervious to attacks of impurities. The addition of antimony lowered the charge voltage for a few cycles, after which, however, the cell regained its normal voltage per-

formance. The antimony was probably deposited and plated over on the negative plate. The other impurities, except silver and platinum, were without perceptible influence upon the voltage characteristics.

When, however, we come to the consideration of the self-discharge of the battery and the life of the active material a much more varied behavior becomes apparent, as will be observed in Table I.

TABLE I.

Effect of Impurities on Self-Discharge and Life of Cells.

Impurity percent of electrolyte wt.	Compound in which introduced	Percent former capacity after standing four weeks	Life Tests Performance of uncontaminated cells considered 100 percent
Magnesium...0.05	$MgSO_4.7H_2O$	92.5	85.7
" ...0.5	Sulphuric acid solution	87.9	79.5
Manganese...0.005	$KMnO_4$	62.8	80.8
" ...0.01	Sulphuric acid	65.4	42.8
" ...0.025	solution	30.1	(1)
" ...0.05		56.5	(1)
" ...0.05	Water	49.2(2)	(1)
" ...0.5	solution	6.15(2)	(1)
Zinc 0.05	$ZnSO_4.7H_2O$	90.0	100.
" 0.5	Water solution	95.5	104.5
Cadmium 0.05	$CdCl_2.2H_2O$	77.2	110.
" 0.5	Water solution	84.1	50.
Iron 0.01	$FeSO_4.7H_2O$	75.	105.2
" 0.05	Water solution	77.75	92.5
" 0.1		77.4	80.4
Nickel.....0.05	$NiSO_4.6H_2O$	76.8	109.
" 0.5	H_2SO_4 solution	76.8	103.5
Tin 0.05	Metallic Tin	85.5	94.95
" .....0.5..	dissolved in sulphuric acid	74.4	92.43
Arsenic.....0.05	As_2O_3 dissolved in HCl, digested with H_2SO_4 to expel Cl	76.	86.7
" 0.5		59.5	86.2
Antimony....0.05	$SbCl_3$ in HCl	71.7	85.5
" 0.5	solution	47.3	51 1

TABLE I—*Continued.*

Impurity percent of electrolyte weight	Compound in which introduced	Percent former capacity after standing four weeks	Life Tests Performance of uncontaminated cells considered 100 percent
Mercury.....0.05	$HgSO_4$	93.5	104.
" 0.5	water solution	92.5	67.75
Silver, 1st test.0.005	$AgNO_3$ in water	74.2	125.6
" " 0.05	solution	83.9	112.9
" " 0.5		59.7	97.5
" 2d test..0.01	$AgNO_3$ Sol.	83.	100.
" " 0.05	digested with	74.3	100.
" " 0.1	H_2SO_4 to expel	69.6	106.8
" " 0.5	nitric acid	33.5	89.5
Platinum...0.00001	$PtCl_4.5H_2O$	....	48.5(3)
" ...0.01	Water solution	....	16.4(3)
Hydrochloric acid.....0.01	HCl	(5)	81.28
" 0.05	"	"	86.3
" 0.1	"	"	96.8
" 0.5	"	"	77.25
" 1.0	"	"	47.3
" 5.0	"	"	20.42
Nitric acid...0.1	HNO_3	81.0	100.8
" ...0.5	"	84.0	98.8
" ...1.0	"	92.5	100.
" ...5.0	"	53.7	(4)
Acetic acid...0.1	$HC_2H_3O_2$	(5)	101.
" ...0.5	"	"	101.8
" ...1.0	"	"	98.
" ...5.0	"	"	36.6
" ..50.(6)	"		

Compounds were added in some instances in 39 percent sulphuric acid solution to prevent altering the specific gravity of electrolyte. All metallic impurities were added one-half hour before completion of charge. Foreign acids were added with original electrolyte on assembly of cells.

(1) Other cells too low to put in life test.
(2) After standing one week.
(3) Loss to these figures in six cycles.
(4) Torn down after standing test. No grid disintegration yet apparent.
(5) Not tested.
(6) Immediate complete sulfation.

The self-discharge or loss of capacity on standing was determined by allowing the cells to stand after charging for intervals of one day, one week and four weeks, respectively, before discharge. They were then discharged at the five-hour rate. Since

the same relative loss in capacity was observed for each of the periods, the loss in capacity for the four-week period only has been recorded. In the third column of the table, this loss is expressed as a percentage of the previously determined capacity of the cell.

The life test consisted of consecutive charges and discharges until the capacity fell to a definite fraction of its former value. Rating the performance of the uncontaminated cells at 100 percent, the relative performance of the contaminated cells is tabulated in column four.

In order to interpret the results of Table I in terms of practical injury to the battery, certain arbitrary assumptions must be made.

First, with respect to self-discharge, a normal or average depreciation of about 18 percent was observed in the uncontaminated cells after standing four weeks. Therefore, we have rated at 100, cells which retained at least 82 percent of their original capacity. Moreover, since normal cells are subject to some variation, we have assumed that no deviation of less than 10 points from the normal thus established can be considered significant.

In like manner, the life of the uncontaminated plates under the experimental conditions was rated at 100, and only a depreciation in excess of 15 percent of this average has been considered significant. The greater margin required for establishing significant differences in the case of the life tests is due to the greater variability of the latter owing to the large number of factors which influence it. The allowances in each case are sufficient to exclude the maximum variations observed in the control cells.

With these assumptions as to what constitutes practical injury, Table II has been prepared. In the first two columns are indicated the minimum amount of the impurity which proved definitely injurious. In the last two columns are given the maximum percentages of the impurity which produced no pronounced deterioration in the cell.

The cells with 0.5 cadmium showed abnormally short life, although the 0.05 cadmium were normal. This is of special interest in connection with the common use of the cadmium electrode in lead battery testing. Further verification is therefore desirable.

The effect of the introduction of antimony was also somewhat surprising, but the result may have been due in part to the hydrochloric acid solution in which it was introduced.

The cases of manganese, silver, and platinum presented striking characteristics.

Manganese as potassium permanganate in water solution was added in quantities of 0.05 and 0.5 percent of the electrolyte weight. There was a steady lessening of capacity with successive discharges immediately following charge until in twenty cycles

TABLE II.

Impurities Added to Storage Batteries.

	Minimum percentage which produced injury.		Maximum percentage which produced no injury	
	Self Discharge	Life	Self Discharge	Life
Magnesium	..	0.5	0.5	0.05
Manganese	0.005	0.005	..	..
Zinc	..	..	0.5	0.5
Cadmium	..	0.5	0.5	0.05
Iron	..	0.1	0.1	0.05
Nickel	..	..	0.5	0.5
Tin	..	..	0.5	0.5
Arsenic	0.5	..	0.05	0.5
Antimony	0.5	0.5	0.05	0.05
Mercury	..	0.5	0.5	0.05
Silver	0.1	..	0.05	0.5
Platinum	not tested	0.00001	..	..
Hydrochloric acid	not tested	1.0	not tested	0.5
Nitric acid	5	..	1.0	1.0
Acetic acid	not tested	5.0	not tested	1.0

after the addition of the manganese the cells had fallen to 83 and 52 percent of their original values for the 0.05 percent and 0.5 percent additions respectively. After a week's standing, the capacity had fallen so low that the cells were torn down and a new series of tests started to confirm the result. Potassium permanganate was then added to correspond to 0.005, 0.01, 0.025, and 0.05 percent of manganese in the electrolyte. All showed an abnormal loss of capacity on standing, and after four weeks those contaminated with 0.025 and 0.05 percent refused to "take charge." The two lower percents gave short life. The positive

plates when examined were expanded, pitted and buckled and the general character of the paste was soft. The negatives were normal.

The addition of silver in water solution of silver nitrate resulted in the immediate precipitation of silver sulphate, shorting the cells and reducing the capacity to 18 percent normal with the 0.5 percent contamination. This capacity was regained with succeeding cycles and in six equalled its former value. A repetition of the test in which the silver nitrate solution was previously digested with sulphuric acid, gave a less marked, although noticeable decrease in initial capacity, which was regained as in the former series. It seems probable that the silver was plated over with spongy lead and rendered less harmful on the negative electrode. However, its effect may be still noted in the loss of capacity on standing.

Platinum gave no room for doubt as to its result. Added even as low as 0.00001 percent, it caused immediate gassing on discharge, and in five cycles of successive charge and discharge the capacity had fallen to 50 percent. On examination, the negatives exhibited a soft, pasty character. The cell voltage on charge failed to rise above 2.37 with a positive to cadmium of 2.42 volts, while the normal cell gives 2.60 as a cell voltage and 2.45 of the positive with respect to cadmium.

Detection of these impurities by other than chemical analysis of the electrolyte is possible only in the cases of manganese, platinum, hydrochloric and acetic acids. Manganese gives the characteristic permanganate color on charge, and the pitted condition of the positive is also an indication. Platinum is distinguished with certainty by gassing of the cell on discharge. Hydrochloric and acetic acids as well as nitric attack the positive grid, but the first two may usually be detected by the odor on charge. Chlorine is evolved from the hydrochloric acid and the characteristic odor of acetic is attendant on that impurity. However, these are not absolute criteria for successive cycles of electrolysis decrease the concentration almost to elimination. Hydrochloric bleaches a wood separator, while with acetic acid there is an unusual growth of lead sulphate crystals around the cell posts.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 28, 1922, President Acheson Smith in the Chair.

ELECTROLYTIC PREPARATION OF ORTHO-AMIDOPHENOL.[1]

By O. W. Brown[2] and J. C. Warner[3]

Abstract.

A brief summary is given of the published work on the electrolytic preparation of ortho-amidophenol. All reductions of ortho-nitrophenol to ortho-amidophenol were carried out in caustic soda solutions and at a copper gauze cathode. Tabulated results of experiments are given which show the effect of current density, concentration of caustic soda and ortho-nitrophenol in the cathode liquor, and temperature at different current densities on current efficiency and material yield. The tabulated results are also expressed graphically by curves. The quantity of amine produced was determined by a method involving diazotization with standard sodium nitrite.

The ordinary chemical methods used in the reduction of nitro compounds to amines have been quite generally applied in the preparation of ortho-amidophenol from the corresponding nitrophenol. The electrolytic method has likewise been the subject of experiments by such investigators as Elbs[4] and Löb.[5]

Elbs based his calculation of yields upon the quantity of hydrogen evolved at the cathode when theoretical quantities of current were employed. He assumed that all of the hydrogen not evolved was used in reducing the nitrophenol to the corresponding amine. Löb prepared ortho-amidophenol by reducing the corresponding nitrophenol in both acid and alkaline solution, and calculated yields from the quantity of amine recovered. Material yields varying

[1] Manuscript received February 18, 1922.

[2] Professor of Chemistry, Indiana University, Bloomington, Ind.

[3] Instructor of Chemistry, Indiana University, Bloomington, Ind.

[4] Jour. fur prakt. chem., 1891 43, 39.

[5] Z. Elekrochem., 1896, 2, 533.

from 50 to 60 percent are claimed for these processes, but, in no case, is there a complete record given of the various factors affecting the reduction.

In this investigation, we have studied the effect of temperature, concentration of sodium hydroxide in the cathode solution, concentration of nitrophenol, and cathodic current density on the reduction of ortho-nitrophenol to ortho-amidophenol in alkaline solution at a copper cathode.

ANALYTICAL.

To eliminate the error which would arise from determining material yields and current efficiencies by recovery of the amine, a direct titration method was used. At the end of each experiment, the cathode solution was transferred to a one liter graduated flask and made to the mark. Portions were then pipetted out for analysis.

In the method of analysis which we used, the amine is diazotized with standard sodium nitrite solution according to the following equation:—

$$C_6H_4OHNH_2 + NaNO_2 + 2HCl = C_6H_4OHN = NCl + NaCl + 2H_2O.$$

Hence one mol of the nitrite is equivalent to one mol of the amine, and 1 cc. of $N/10$ $NaNO_2$ (standardized against $KMnO_4$) is equivalent to 0.00545 gram of ortho-amidophenol.

Ten to 50 cc. of the alkaline amidophenol solution were transferred, by means of a pipette, to a 300 cc. beaker. Twenty-five cc. of HCl (1 : 1) and sufficient H_2O to make a total volume of 150 cc. were added. The standard nitrite solution was then slowly added from a burette until a drop of the solution produced a blue coloration on starch iodide paper. In dilute solutions, the titration can be carried out at room temperatures.

EXPERIMENTAL.

In all our experiments, copper gauze cathodes were used. The container was a beaker about 13 cm. high and 9 cm. in diameter. A porous cup, 10.8 cm. high and 5.0 cm. in diameter, contained a 1.4 dm^2 (counting both sides) iron wire gauze anode and the anode solution, which in all experiments consisted of 100-125 cc.

of 15 percent caustic soda. The cathode, in all experiments except those recorded in Table III, consisted of 18-mesh copper gauze having a surface of 1.0 dm^2 (counting both sides). The gauze was made of wires 0.041 cm. in diameter.

The temperature of electrolyte was regulated by means of an electric hot plate beneath the beaker and glass cooling coils in the cathode compartment, through which water could be circulated. The current strength was measured by an ammeter graduated to 0.05 ampere. The cathode solution was agitated by means of a glass stirrer run by a small electric motor. The ortho-nitrophenol used in our experiments was purified by steam distillation and then dried. Its melting point was 44-45° C.

In the following table, results of experiments showing the effect of cathode current density on current efficiency are recorded.

TABLE I

Effect of Cathodic Current Density

Cathode solution: 300 cc. 15 percent NaOH; 5 gm. o-nitrophenol.
Temperature: 62° ± 2° C.
Ampere hours used: 5.78 (theory).

Cathodic C. D. amp. per. dm^2	Voltage drop through cell Five min. after start.	Material yield and current efficiency. Percent	Average material yield and current efficiency. Percent
1 1	2.0 1.9	96.6 96.4	96.5
2 2	3.1 3.0	95.9 96.3	96.1
4 4	3.4 3.4	94.1 94.2	94.2
6 6	4.3	91.6 92.1	91.8
10 10	4.8 4.6	84.4 84.1	84.2

The data given in Table I are shown graphically in Fig. 1. It can readily be seen that an increase of the current density from one to ten amperes per square decimeter causes a regular decrease in the current efficiency and material yield of ortho-amidophenol.

With low current densities, hydrogen evolution at the cathode started only a few minutes before the theoretical number of ampere hours had passed. With higher current densities, it started several minutes earlier and the cathode liquor was still yellow due to the remaining o-nitrophenol. Due to these observations, a study was made of the current efficiency over successive periods of the reduction process.

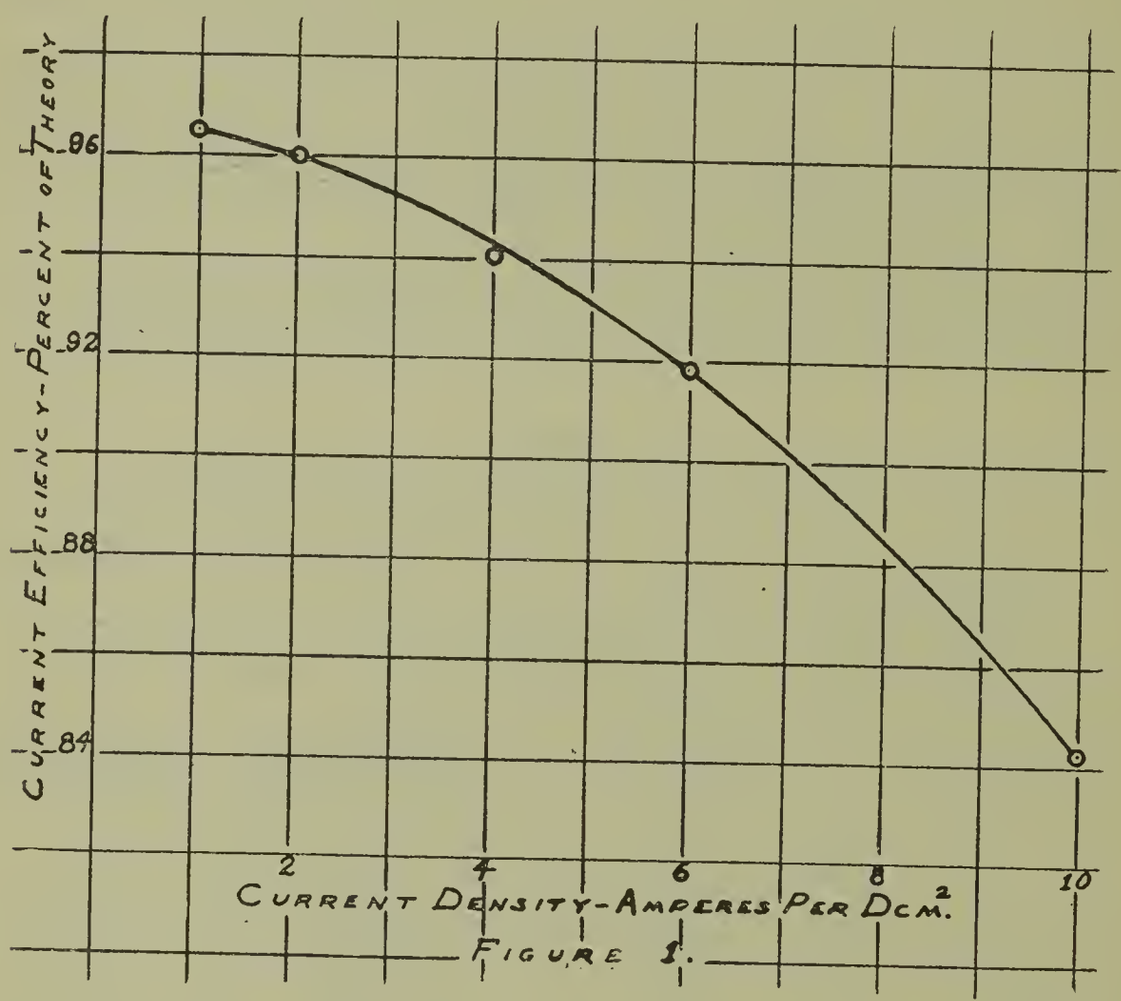


Figure 1.

Theoretically, to reduce 5 grams of o-nitrophenol, 5.78 ampere hours are required. The reduction was divided into four equal periods, and the average current efficiency over each period determined. The current, in these experiments, was regulated by adjusting small changes shown by an ammeter in the line, but was accurately measured by means of a copper coulometer.

In Table II, the results of experiments showing the current efficiency during successive periods of the reduction process at several current densities are given.

The results from Table II are plotted in Figure 2. From the data, it is evident that the current efficiency over successive periods

of the reduction process drops much more rapidly at a high current density than at low ones. However, almost theoretical efficiency can be obtained with a current density of 10.0 amperes per square decimeter as long as the o-nitrophenol concentration in the cathode solution is as high as 1.0 gram per 100 cc.

TABLE II

Current Efficiency at Different Current Densities.

Cathode solution: 300 cc. 15 percent NaOH; 5 grams o-nitrophenol.
Temperature: 62-64° C.

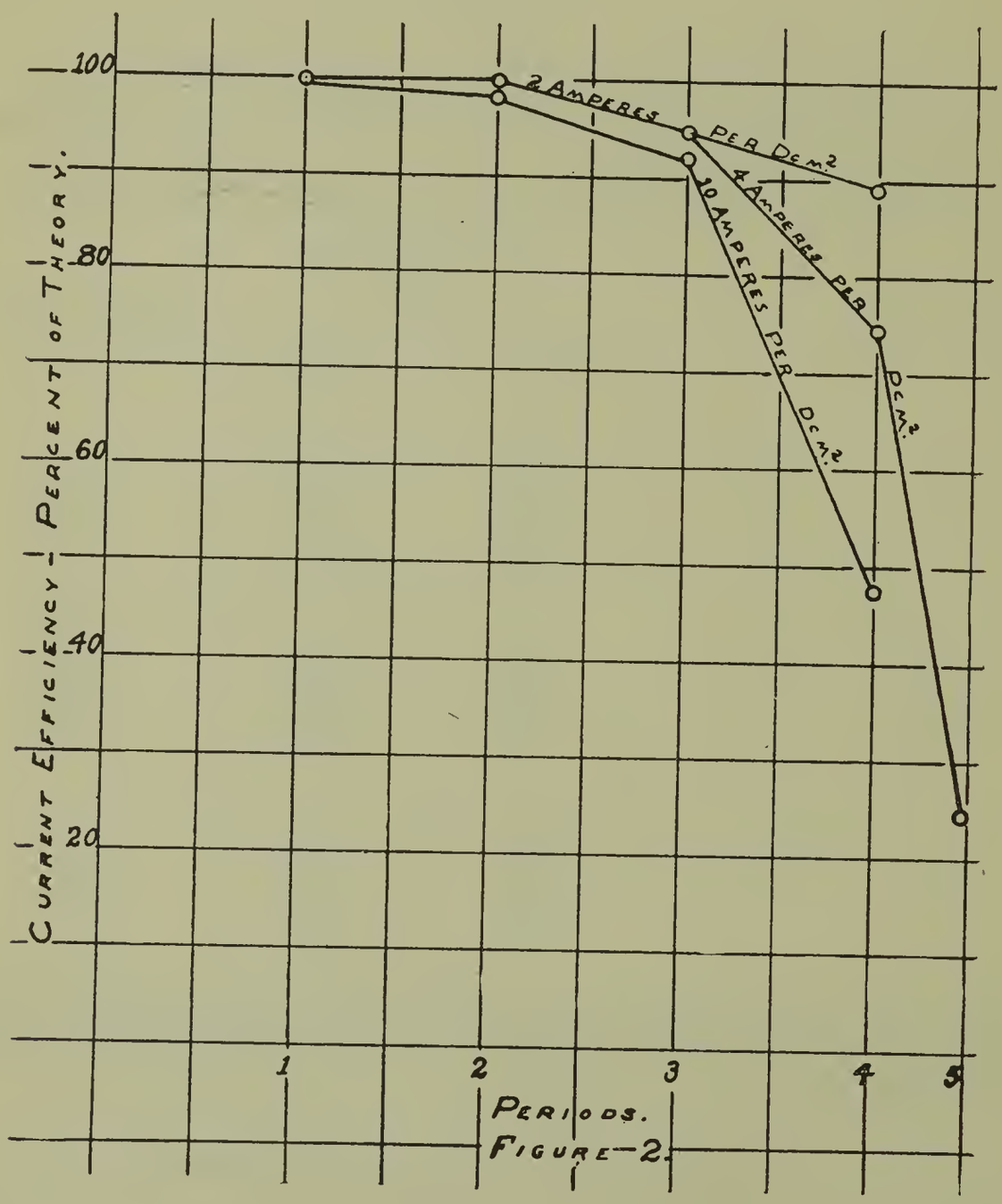
Cathodic C. D. Amp. per. dm.^{2}	Period	Gm. o-nitrophenol in 100 cc. of cathode solution		Average current efficiency over period. Percent
		Beginning of period	End of period	
2.0	1	1.666	1.245	100.0
	2	1.245	0.830	100.0
	3	0.830	0.436	94.9
	4	0.436	0.065	89.3
4.0	1	1.666	1.245	99.8
	2	1.245	0.830	100.0
	3	0.830	0.436	94.9
	4	0.436	0.127	74.6
	5*	0.127	0.025	24.7
10.0	1	1.666	1.253	99.6
	2	1.253	0.846	98.2
	3	0.846	0.463	92.2
	4	0.463	0.265	47.7

*Each of the first four periods represent 25 percent of the time theoretically required to reduce the 5 grams of o-nitrophenol. Period 5, in the experiments with a current density of 4.0 amperes per square decimeter, represents time 10.4 percent in excess of theory.

The results of the experiments recorded in Table III show the relation between concentration of caustic soda in the cathode solution and current efficiency.

The results in Table III are shown graphically in Figure 3. Current efficiencies increase with increased concentration of caustic soda in the cathode solution until a concentration of 15 percent of NaOH is reached. From this point the current effi-

ciency decreases due to decreased solubility of the sodium salt of o-nitrophenol in the caustic liquor. The second reduction carried out in 20 percent NaOH resulted in a higher current efficiency because the sodium salt of the nitrophenol was produced in a finely divided condition by grinding the nitrophenol in a solution of caustic soda.



Figure—2.

It is also interesting to note that the concentration of caustic soda giving the highest current efficiency corresponds to the caustic soda solution having the minimum resistance. Other factors, however, seem to have a greater influence on the potential drop over the cell than the resistance of the electrolyte.

In Tables IV and V, the results of experiments are recorded which show the relation between temperature of the cathode solution and current efficiency.

The results from Tables IV and V are shown graphically in Figure 4. At high current densities, current efficiency is directly proportional to temperature. With lower current densities, current efficiency inceases with temperature up to about 60° C. Further increases in temperature have no effect on current efficiencies. The first experiments of this series at 30° C. (not recorded) gave low and inconsistent results because the o-nitrophenol did not completely dissolve in the electrolyte. When the cathode solution containing the nitrophenol was heated to 60-80°

TABLE III

Effect of Concentration of Caustic Soda

Cathode: Copper gauze, 24-mesh, made of wires 0.031 cm. in diam. 4.1 dm.^{2} (counting both sides).
Cathode solution: 425 cc. NaOH solution; 15 grams o-nitrophenol.
Cathodic current density: 3.16 amperes per dm^2.
Ampere hours used: 17.29 (theory).
Temperature: 62-64° C.

Conc. NaOH in cathode soln. Percent by weight	Voltage drop through cell. Five min. after start.	Material yield and current efficiency. Percent	Avg. Material yield and current efficiency. Percent
2	6.0	87.6	87.5
2	5.8	87.4	
5		94.7	94.9
5		95.0	
5		95.0	
10	6.4	98.3	97.9
10	6.4	98.3	
10	6.5	97.3	
15	7.0	99.5	99.3
15	7.1	99.4	
15	7.0	99.0	
20	7.0	90.3	
20	6.9	94.1	
30	8.4	11.8	11.7
30		11.6	

C. and then cooled to 30°C., previous to starting the reduction the nitrophenol all remained in solution and consistent results were obtained.

The relation between concentration of o-nitrophenol in the

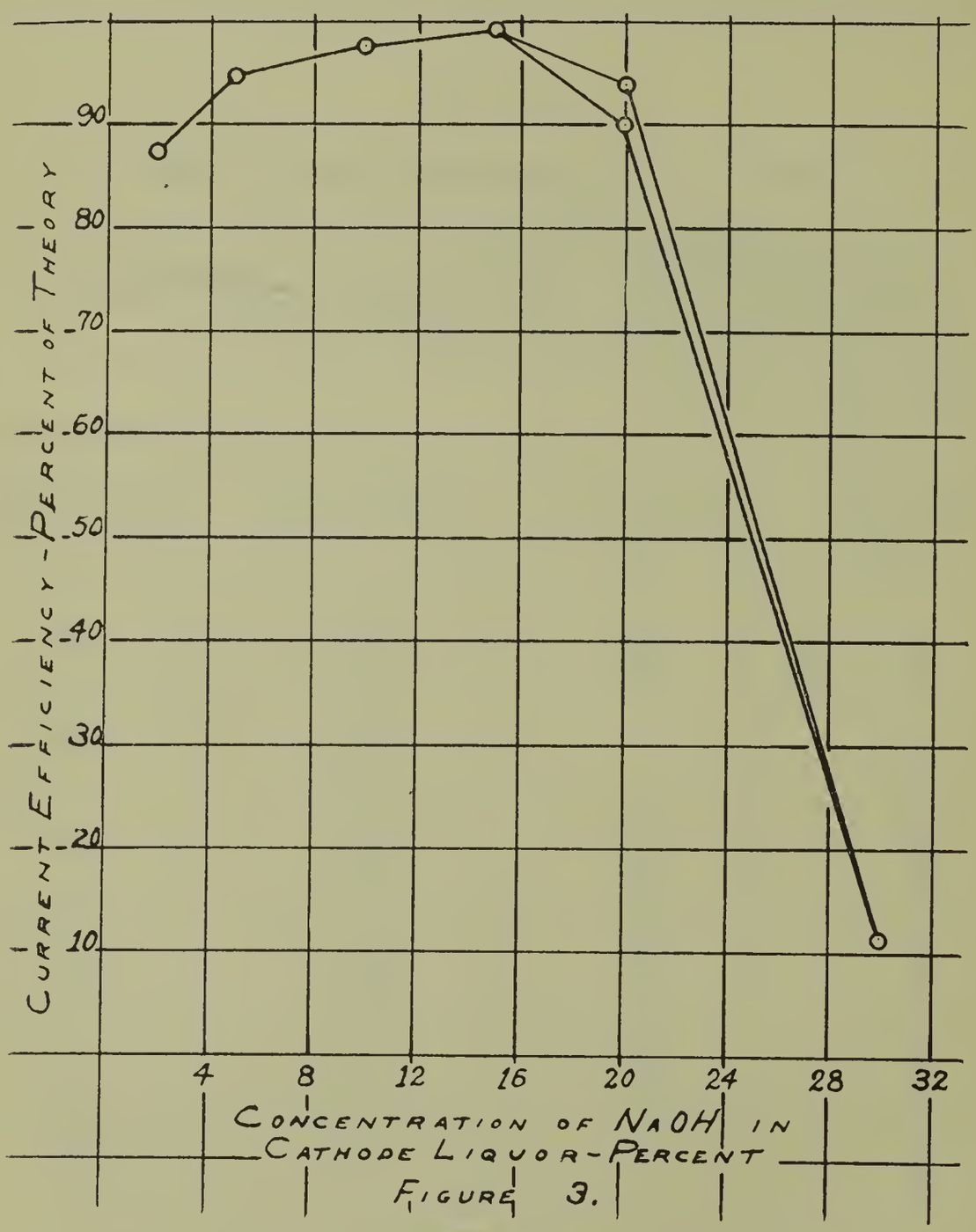


Figure 3.

cathode solution and current efficiency is shown by the experiments recorded in Table VI.

The results from Table VI are plotted in Figure 5. Current efficiency increases quite rapidly until a concentration of o-nitrophenol of about 2.8 grams per 100 cc. of cathode solution is reached. Further increases in concentration have little effect on

TABLE IV.

Effect of Temperature on Current Efficiency

Cathode solution: 300 cc. 15 percent NaOH; 5 grams o-nitrophenol.
Current density: 10 amp. per dm^2.
Ampere hours used: 5.78 (theory).

Temperature °C.	Voltage through cell Five min. after start	Material yield and current efficiency. Percent
30	5.2	80.3
33	5.2	81.0
50	3.9	83.2
52	4.3	83.8
62*	4.7	84.2
75	3.4	86.7
75	3.5	87.2
95	3.2	89.7
95	3.7	90.4

*The experiment at 62°C. is taken from Table I.

TABLE V.

Effect of Temperature on Current Efficiency.

Cathode solution: 300 cc. 15 percent NaOH; 5 grams o-nitrophenol.
Current density: 4.0 amp. per dm^2.
Ampere hours used: 5.78 (theory).

Temperature °C.	Material yield and current efficiency Percent	Voltage drop through cell. Five min. after start	Avg. material yield and current efficiency. Percent
30	3.8	89.4	89.5
30	3.7	89.7	
50	2.5	92.6	92.5
50	2.5	92.4	
60*	3.0	94.2	94.2
75	2.5	94.0	93.8
75	2.3	93.7	
95	2.3	94.0	93.9
95	2.5	93.8	

*The experiment at 62°C was taken from Table I.

current efficiency, probably due to increased loss due to diffusion through the porous cup when the concentration is increased and the time reduction lengthened. The limiting concentration is

practically reached with 5 grams of o-nitrophenol in 100 cc. of cathode liquor, for it is only with difficulty that this quantity of the nitrophenol can be dissolved in 100 cc. of 15 percent caustic soda.

Due to the low solubility of the sodium salt of o-nitrophenol in caustic soda solutions, it was thought that possibly there would be some advantage in adding o-nitrophenol in smaller amounts at

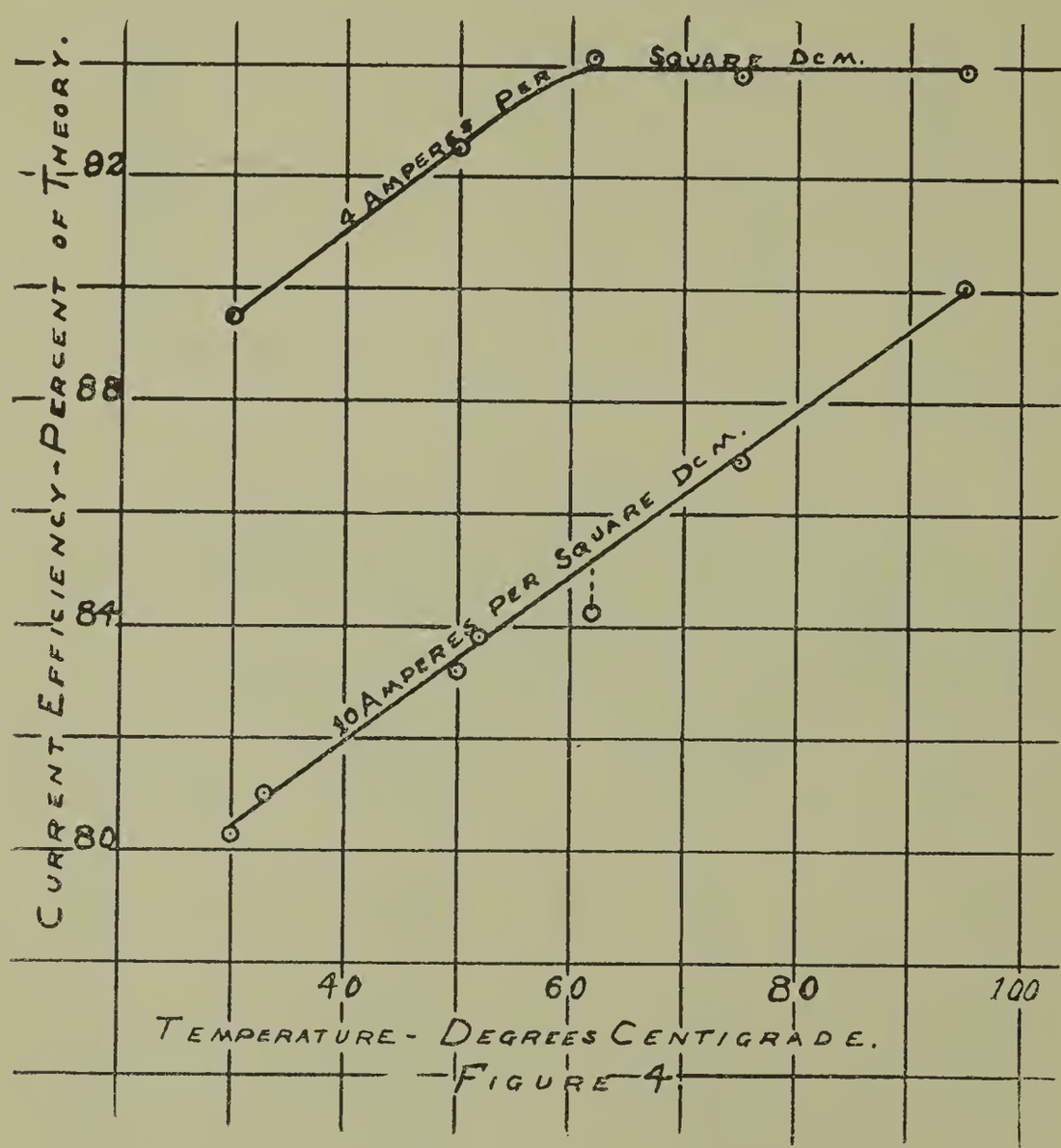


Figure 4.

intervals. In this way, an attempt was made to reduce more o-nitrophenol with a given volume of cathode solution than could initially be dissolved. The results of these experiments are recorded in Table VII.

The results of these experiments show that by adding a part of the o-nitrophenol at intervals during the reduction process, a double quantity of o-nitrophenol can be reduced in a given volume

Table VI

Effect of Concentration of O-nitrophenol

Cathode solution: 300 cc. 15 percent NaOH; varying quantities of o-nitrophenol.

Cathodic current density: 6.0 amp. per dm^2.

Temperature: 62-64° C.

Gm. o-nitrophenol in 300 cc. of cathode solution	Voltage drop through cell. 5 min. after start	Ampere-hours used.	Material yield and current efficiency. Percent	Av. Material yield and efficiency. Percent
2 2	3.3 3.1	2.31 2.31	86.3 86.7	86.4
5 5	4.3	5.78 5.78	91.6 92.1	91.8
8 8	5.3	9.25 9.25	94.2 95.0	94.6
10 10	5.0 6.0	11.56 11.56	94.5 94.5	94.5
12 12	4.2 4.5	13.87 13.87	94.7 94.4	94.5
15 15	3.3 3.3	17.30 17.30	94.6 95.4	95.0

Table VII

Addition of O-nitrophenol at Intervals

Cathode solution: 300 cc. 15 percent. NaOH; varying quantities of o-nitrophenol.

Cathodic current density: 10.0 amp. per dm^2.

Temperature: 62-64° C.

O-nitrophenol added to 300 cc. of cathode solution. Grams.			Total ampere hours used Theory.	Material yield and current efficiency. Percent
At start	After passing 5.78 ampere hours	After passing 11.56 ampere hours		
10	0.00	0.00	11.56	92.0
10	0.00	0.00	11.56	92.6
10	0.00	0.00	11.56	91.7
10	5.00	5.00	23.12	91.7
10	5.00	5.00	23.12	91.1

of cathode solution with practically the same current efficiency. Experiments have shown, however, that if the addition of o-nitrophenol is continued over a more extended period, the current efficiency becomes lower, due to diffusion through the porous cup into the anode compartment.

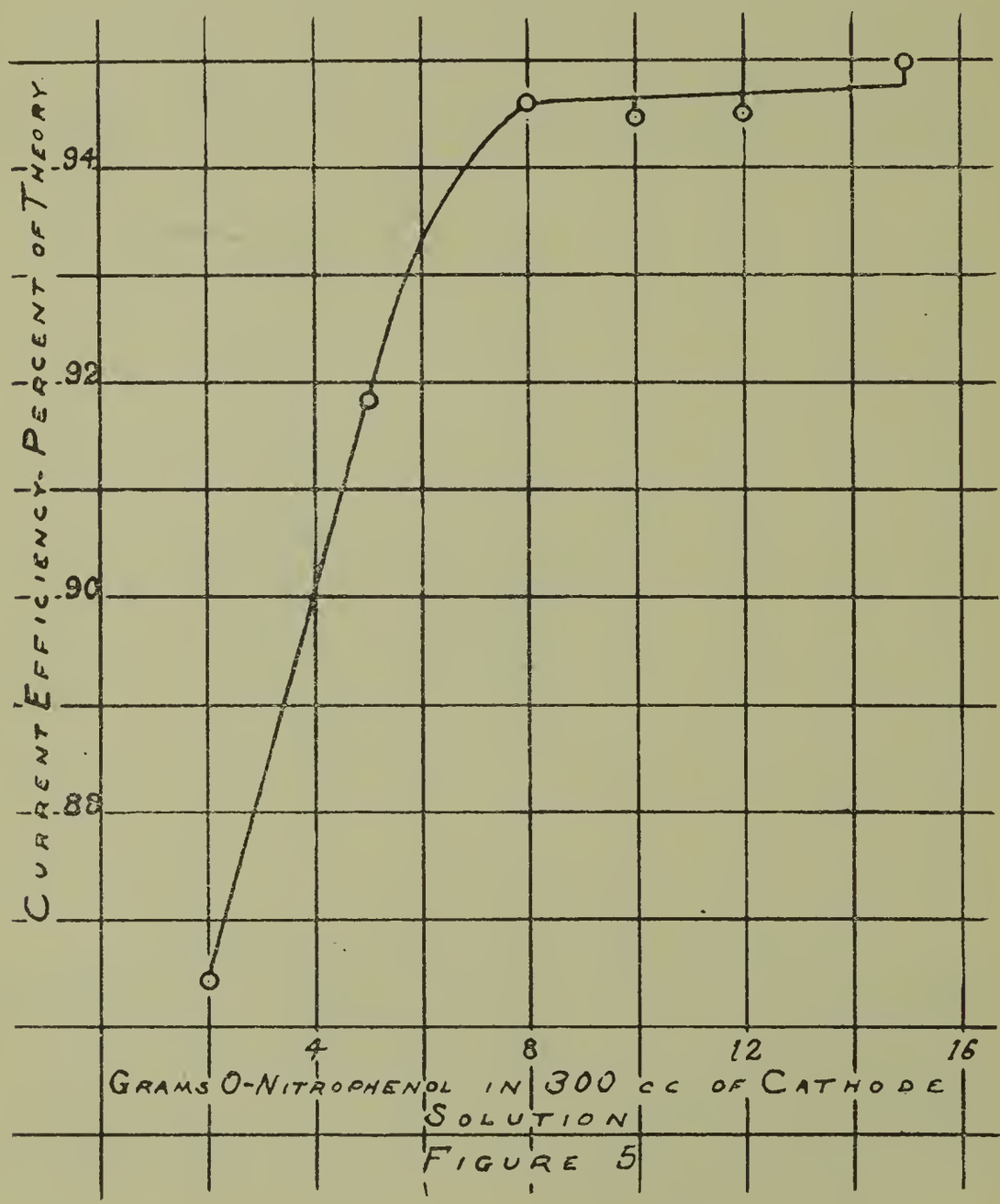


Figure 5

The concentration of o-amidophenol in the cathode solution is an important consideration from the point of view of recovery of the amine from its solutions. The quantity of the amine lost in the mother liquor will remain practically constant, hence with more concentrated solutions the percentage loss in the mother liquor will be lower.

The authors have found the following method to be quite

satisfactory for the recovery of o-amidophenol from its alkaline solutions. Concentrate the alkaline solution by heating on a steam bath until the caustic soda concentration reaches 10-15 grams in 100 cc. Cool and liberate the amine by passing CO_2 through the solution. The o-amidophenol which separates as small plate-like crystals may then be separated from the mother liquor by filtration and further purified by washing on the filter several times with cold water.

When this procedure was used to recover o-amidophenol from solutions containing approximately 3 to 4 grams of the amine in 100 cc. of solution, a recovery of about 90 percent was obtained. The purity of this material was 97 to 99 percent.

The relative merits of various metals as cathode materials and the best methods for recovering o-amidophenol from solutions will be discussed in following articles.

CONCLUSIONS.

1. An electrolyte containing 15 percent NaOH gives highest current efficiencies and highest material yields of o-amidophenol.

2. The solubility of the sodium salt of o-nitrophenol in caustic soda solutions decreases as the concentration of caustic soda increases.

3. A concentration of 3 to 5 percent of o-nitrophenol in the cathode solution gives the highest current efficiencies and material yields.

4. When current densities of 10.0 amperes per dm^2 or above are used, the temperature of the electrolyte should be kept near the boiling point. When current densities of 4.0 amperes per dm^2 or lower are used, there is no advantage in maintaining the temperature of the electrolyte above 60°C.

5. With a current density of 4.0 amperes per dm^2 or lower, 100 percent current efficiencies can be obtained as long as the concentration of o-nitrophenol does not fall below 0.8 gram per 100 cc. of cathode solution.

6. As best conditions for the electrolytic preparation of o-amidophenol from o-nitrophenol in alkaline solution and at a copper cathode, the following conditions are recommended. Start the reduction with a cathode solution of 15 percent NaOH containing

3 to 5 grams of o-nitrophenol per 100 cc. Maintain a temperature slightly below the boiling point and use a current density of 10 amperes per dm.^{2} When one half of the nitrophenol has been reduced, add one half the original amount of the nitro compound. After another such period, add a similar amount of o-nitrophenol. Continue the reduction with a current density of 10.0 amperes per dm^2 until the concentration of o-nitrophenol has dropped to about 1.5 grams in 100 cc, then lower the current density to 4 to 5 amp. per dm^2 and the temperature to 60 to 70° C, and continue the electrolysis until the concentration of o-nitrophenol has dropped to 0.8 gram per 100 cc. Finish the reduction with a current density of 1 to 2 amperes per dm.^{2} Under these conditions, a material yield and current efficiency of 97 to 99 percent should be obtained.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

THE ELECTROLYTIC GENERATION OF HYDROGEN AND OXYGEN WITH SPECIAL REFERENCE TO THE UTILIZATION OF OFF-PEAK POWER.[1]

By Wm. G. Allan[2]

Abstract.

This paper deals with the electrolytic dissociation of water into its elementary gases, hydrogen and oxygen. The economics of the problem are set forth in such a form that the costs of the gases, under widely varying conditions as to the cost of electrical energy, rates for depreciation, and current density, can be ascertained off-hand by reference to a series of curves. The utilization of "off-peak" power, for the purpose of generating these gases at cheap prices with a view to their use in large quantities in the chemical or other industries, is advocated. Special mention is made with a brief description and some illustrations of a new type of electrolytic cell, designed and developed by the author. Basic constants and data used in calculations are given, and comparisons of the chief characteristics of the new cell with those of other existing types are contained in a series of tables.

The new type of cell is adapted to operate under widely varying conditions of current density per square inch of projected electrode area, without too great a sacrifice of energy efficiency. It is thus adapted for operation at different rates of gas production, according to the cost of power at any particular time of a 24-hour day, during which it is conceivable that a power consumer has contracted for power under two or more different rates. The higher the rate of gas production, the less the influence of the fixed charges in the total cost of the gases, while depreciation does not increase at a rate which is proportionate to the rate of gas production. As a result, at high current densities, the cost of power

[1] Manuscript received February 11, 1922.

[2] Electrical and Research Engineer, Toronto Power Co., Ltd., Toronto, Canada.

becomes the major item in the total costs of the gases, and where power is cheap, as in the case of "off-peak" power, the gases may be produced very cheaply, and many processes which, up to the present, have been excluded from consideration now come at least within the range of possibility, while others are definitely placed in the class of commercially feasible processes. The paper endeavors to show the influence and relative importance of the various items entering into the costs of the gases, and finally lists the present and future possible uses of the two gases.

In discussing the question of the electrolytic decomposition of water, and the generation of hydrogen and oxygen gases therefrom, it will be well at the outset to give the basic data and constants which have been used in any calculations. This is all the more necessary because, on looking into the matter, it will be found that different investigators have given different values to the various constants and data involved, and while such differences are not perhaps very great, they are nevertheless sufficient to produce fairly wide differences in results of some of the calculations made from their use.

The writer does not make a claim that the figures of basic constants and data used are absolutely correct beyond question, but merely that they are the most accurate known to him and are taken from sources which bear a certain authority. Not only so, but any one criticising any of the results may check back to the original data and constants, and where more accurate figures are available, may substitute the same, and make the necessary corrections. The figures used by the writer are given on the next page.

From the data and constants as stated, the voltage which would represent 100 percent energy efficiency is calculated to be 1.496 volts.

The energy efficiency can also be expressed in cubic feet of both gases or of either gas per K. W. H. which at 100 percent will be 15.87 cu. ft. of both gases per K. W. H., approximately in the proportion of 2 volumes of hydrogen to 1 of oxygen; *i. e.,* 10.58 cu. ft. of hydrogen and 5.29 cu. ft. of oxygen per K. W. H., the volumes being correct at 20° C. and 760 mm. pressure.

Basic Constants and Data Used.

One Faraday	= 96,500 coulombs.
Density of Hydrogen Gas.....	= 0.005621 lb. per cu. ft. at 0° C. and 760 mm. pressure (Smithsonian Tables 1918, 6th Edition, Table No. 69, p. 91).
Electrochemical Equivalent of Hydrogen (valence = 1).....	= 0.0376 g. per amp-hr. = 0.00008289 lb. per amp.-hr. = 0.014747 cu. ft. (at 0° C. and 760 mm. pressure) per amp.-hr.
Coefficient of Expansion of Hydrogen per °C. between 0° and 100° at or around 760 mm. pressure....	= 0.00366.
Electrochemical Equivalent of Hydrogen in cu. ft. at 20° C. and 760 mm. pressure per 1,000 amp.-hr....	= 15.8266 cu. ft.
Density of Oxygen Gas.....	= 0.08922 lb. per cu. ft. at 0° C. and 760 mm. pressure (Smithsonian Tables 1918, 6th Edition, Table No. 69, p. 91).
Electrochemical Equivalent of Oxygen (valence = 2).....	= 0.2984 g. per amp.-hr. = 0.00065786 lb. per amp.-hr. = 0.00737344 cu. ft. (at 0° C. and 760 mm. pressure) per amp.-hr.
Coefficient of Expansion of Oxygen per °C. between 0° and 100° C. at or around 760 mm. pressure.....	= 0.0036681.
Electrochemical Equivalent of Oxygen in cu. ft. at 20° C. and 760 mm. pressure per 1,000 amp-hr...	= 7.9144 cu. ft.
Heat of formation of liquid water from gaseous Hydrogen and Oxygen per gram equivalent.....	= 69,000 gram-calories.
One gram-calorie	= 4.184 joules (watt-seconds).

Table I has been prepared to show the relation between energy efficiency expressed as a percentage, and expressed in cubic feet of both or either gas per K. W. H., and also expressed in volts per cell assuming 100 percent current efficiency. The current efficiency is 100 percent when no products other than oxygen and hydrogen gas are produced, and when there is no re-diffusion of the gases or ions throughout the electrolyte or losses in any

other way. Such conditions are obtainable with correct design of the cells and their parts.

TABLE I.

Efficiency of Electrolytic Oxy-Hydrogen Cells

Energy Efficiency in Percent	Cubic Feet of Gas per K. W. H.			Voltage Per Cell at 100 percent Current Efficiency Corresponding
	Both Gases	Hydrogen	Oxygen	
100	15.87	10.58	5.29	1.496
95	15.07	10.05	5.02	1.575
90	14.28	9.52	4.76	1.662
85	13.49	8.99	4.50	1.760
80	12.70	8.46	4.24	1.870
75	11.90	7.94	3.96	1.995
70	11.11	7.41	3.70	2.137
65	10.32	6.88	3.44	2.300
60	9.52	6.35	3.17	2.493
55	8.73	5.82	2.91	2.720
50	7.935	5.29	2.645	2.980
45	7.14	4.76	2.38	3.324
40	6.35	4.23	2.12	3.740

Expressed in yet another way, the energy required per 1,000 cu. ft. of both or either gas at 100 percent energy efficiency may be stated. This is

1,000 cu. ft. of both gases in the ratio of 2 to 1 of H_2 to O_2 will require 63.012 K. W. H.

or

1,000 cu. ft. of H_2 and 500 cu. ft. of O_2 will require 94.518 K. W. H.

Table II, giving the cost of electrical energy per 1,000 cu. ft. of hydrogen and per 500 cu. ft. of oxygen, *i. e.*, per 1,500 cu. ft. of both gases, at different energy efficiencies from 100 down to 40 percent at different rates for power, may be found useful.

The decomposition of water into its elementary gases, hydrogen and oxygen, by electrolysis, is an ideal means for the utilization of electrical energy, and one which is destined to come into greater use as the demand for the gases increases, and as the apparatus for its successful accomplishment is improved and brought to a higher state of perfection. A survey of the different makes and types of electrolytic cells on the market, at least up

TABLE II

Costs of Electrical Energy Expressed in Cents Per 1,000 Cu. Ft. of Hydrogen and 500 Cu. Ft. of Oxygen, i. e., Per 1,500 Cu. Ft. of Both Gases.

Cost of Energy per K. W. H.	Percentage Energy Efficiency												
	100	95	90	85	80	75	70	65	60	55	50	45	40
1 mill.....	9.452	9.95	10.5	11.12	11.815	12.6	13.5	14.54	15.75	17.2	18.9	21.0	23.63
1.5 mills....	14.178	14.925	15.75	16.68	17.722	18.9	20.25	21.81	23.625	25.8	28.35	31.5	35.445
2 "	18.904	19.9	21.0	22.24	23.63	25.2	27.0	29.08	31.5	34.4	37.8	42.0	47.26
2.5 "	23.63	24.875	26.25	27.80	29.537	31.5	33.75	36.35	39.375	43.0	47.25	52.5	59.075
3 "	28.356	29.85	31.5	33.36	35.445	37.8	40.5	43.62	47.25	51.6	56.7	63.0	70.89
3.5 "	33.082	34.825	36.75	38.92	41.352	44.1	47.25	50.89	55.125	60.2	66.15	73.5	82.705
4 "	37.808	39.8	42.0	44.48	47.26	50.4	54.0	58.16	63.0	68.8	75.6	84.0	94.52
4.5 "	42.534	44.775	47.25	50.04	53.167	56.7	60.75	65.43	70.875	77.4	85.05	94.5	106.335
5 "	47.26	49.75	52.5	55.60	59.075	63.0	67.5	72.7	78.75	86.0	94.5	105.0	118.15
5.5 "	51.986	54.725	57.75	61.16	64.982	69.3	74.25	79.97	86.625	94.6	103.95	115.5	129.965
6 "	56.712	59.7	63.0	66.72	70.89	75.6	81.0	87.24	94.5	103.2	113.4	126.0	141.78
6.5 "	61.438	64.675	68.25	72.28	76.797	81.9	87.75	94.51	102.375	111.8	122.85	136.5	153.595
7 "	66.164	69.65	73.5	77.84	82.704	88.2	94.5	101.78	110.25	120.4	132.3	147.0	165.41
7.5 "	70.89	74.625	78.75	83.40	88.611	94.5	101.25	109.05	118.125	129.0	141.75	157.5	177.225
8 "	75.616	79.6	84.0	88.96	94.52	100.8	108.0	116.32	126.0	137.6	151.2	168.0	189.04
8.5 "	80.342	84.575	89.25	94.52	100.427	107.1	114.75	123.59	133.875	146.2	160.65	178.5	200.855
9 "	85.068	89.55	94.5	100.08	106.334	113.4	121.5	130.86	141.75	154.8	170.1	189.0	212.67
9.5 "	89.794	94.525	99.75	105.64	112.241	119.7	128.25	138.13	149.625	163.4	179.55	199.5	224.485
1 cent....	94.52	99.5	105.0	111.2	118.15	126.0	135.0	145.4	157.5	172.0	189.0	210.0	236.3
1.5 cents...	141.78	149.25	157.5	166.8	177.22	189.0	202.5	218.1	236.25	258.0	283.5	315.0	354.45
2 " ...	189.04	199.0	210.0	222.4	263.3	252.0	270.0	290.8	315.0	344.0	378.0	420.0	472.6
3 " ...	283.56	298.5	315.0	333.6	354.45	378.0	405.0	436.2	472.5	516.0	567.0	630.0	708.9

until very recently, indicates that such cells are not well adapted for the purpose and possess some serious disadvantages, such as enormous floor space occupied, great weight not only of the cells themselves but also of the electrolyte contained in them, not to mention their high first cost and the, relatively speaking, low energy efficiency of the process carried out by them. Perhaps the most vital disadvantage possessed by such cells is their lack of flexibility to different conditions of operation. They are usually designed to operate under fixed conditions as to cost of energy, quantity of gas to be produced in a given time and the amount of such electrical energy to be absorbed by the cells.

The author will try to show that oxy-hydrogen electrolytic cells should be able to accommodate themselves to widely varying conditions, in both the available amount and the cost of the electrical energy, using at one period of a 24-hour day a large amount of cheap "off-peak" power, and at another period of the same 24-hour day, a smaller amount of electrical energy, such as "firm" power, costing more per K. W. H., while there may also be intermediate periods when both the amount and the cost of the energy used is between the maximum and the minimum mentioned above.

It is well known to the electrical engineer that contracts for the supply of electrical energy may be made between a power-user and supply company, to which widely varying conditions will apply. For example, a power-user may contract to use a certain amount of "firm" power at, say $50 per horse-power year, said power being available 24 hours per day, that is, at any time it is called for. He may, at the same time, contract for, say, "12-hour" power, *i. e.,* available at certain times during 12 hours out of the 24 in a day, and this power might cost him, for example, $25 per horse-power-year. As a third possibility, a power-user may also contract for the use of so-called "off-peak" power, which will be available during periods of "off-peak," such periods enduring for possibly 5 or 6 hours out of the 24, and such power might conceivably be had for $12.50 per horse-power-year.

The "firm" power would be available at the power-user's demand, and the amount used and the time when used would be under his control. The "12-hour" power would be partly under

the control of the power-user and partly under the control of the supply company. It would be available in certain amounts at certain stipulated times. The "off-peak" power would, as to both the amount used and the time when used, be to a larger extent under the control of the supply company, seeing that such power would only be available when the demand from other users was at a minimum.

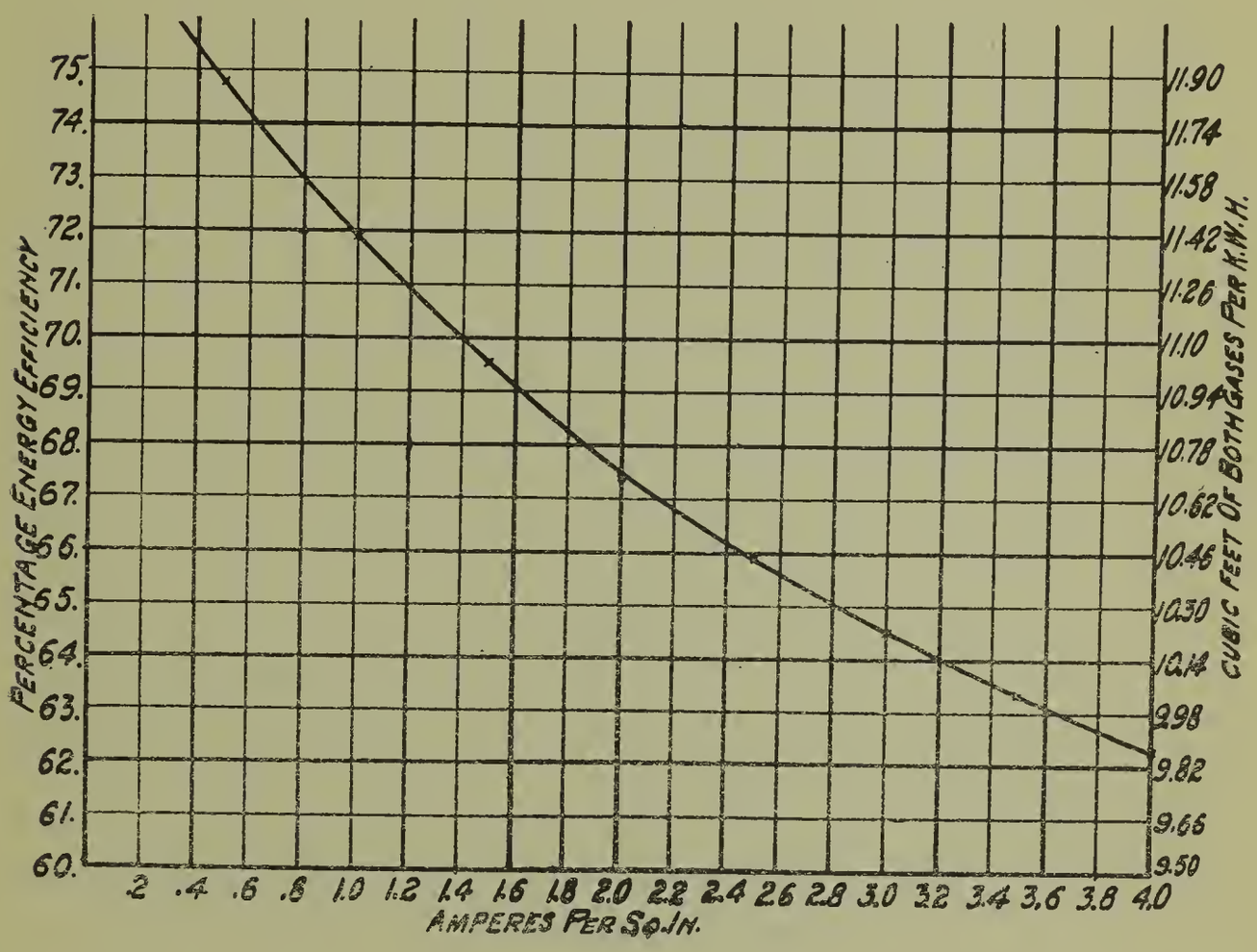


FIG. 1

To a power-user having an oxy-hydrogen electrolytic cell plant, it would obviously be highly desirable if he were able to operate his entire plant at different times throughout a 24-hour day under any one or all of the above conditions. In this way his fixed charges would be reduced to a minimum when spread over all the gas produced. To do this, however, the cells would have to be capable of operating over a wide range of current without too great a sacrifice of efficiency at the higher currents, and without involving prohibitive depreciation charges.

A type of oxy-hydrogen electrolytic cell will be described,

which has been designed and developed by the author as a result of research work carried on during several years past. This cell will operate from low current densities, of, say, about half an ampere per square inch of projected electrode area up to 3 or even 4 amperes per square inch, and the energy efficiencies over this range of current are given on the attached curve. (Fig. 1). It will be noted that they range from 74.8 percent (7.92 cu. ft. of

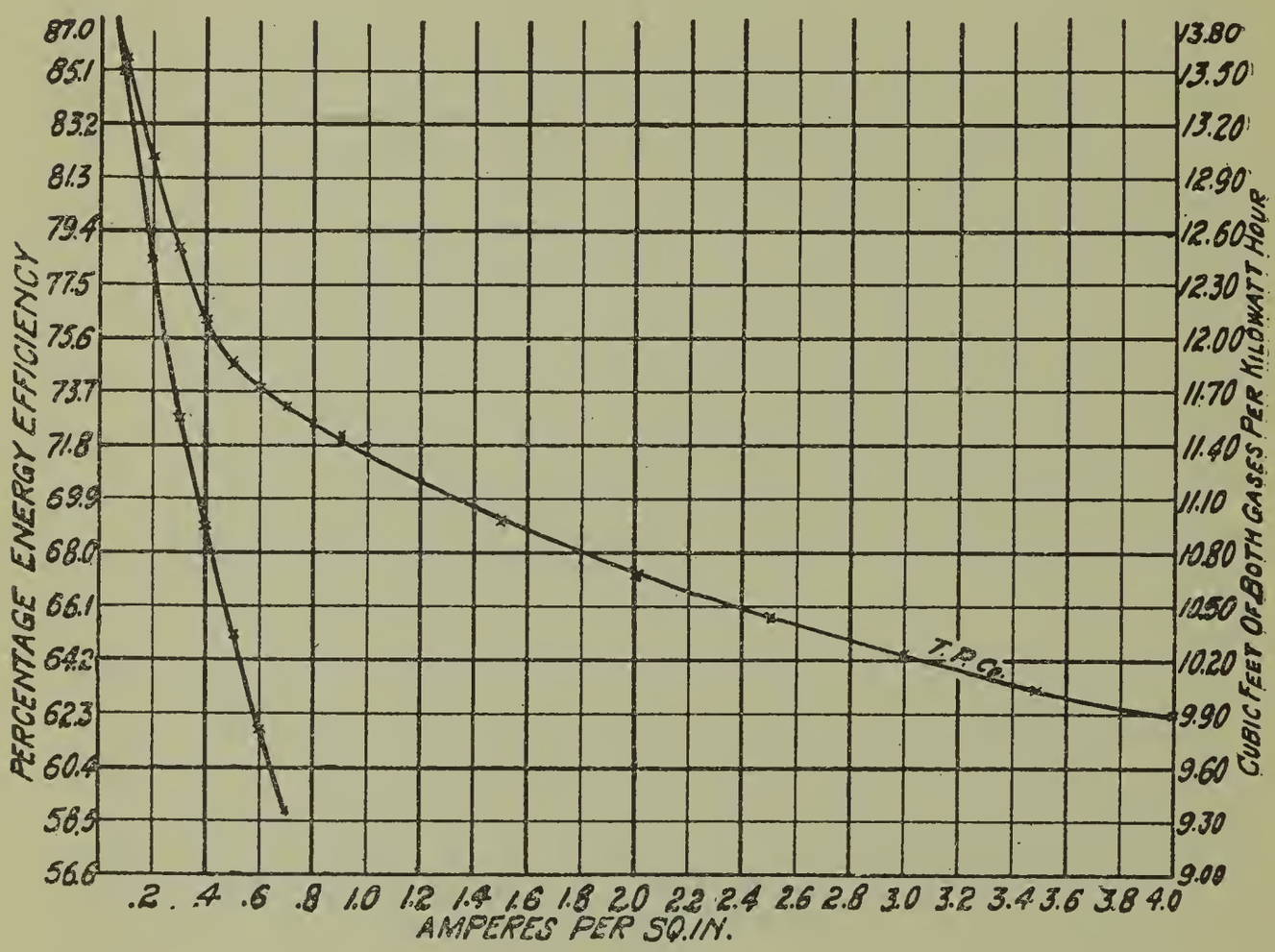


Fig. 2.

hydrogen and 3.95 cu. ft. of oxygen per K. W. H.) at 0.5 of an ampere per sq. in., to 62.33 percent (6.59 cu. ft. of hydrogen and 3.30 cu. ft. of oxygen per K. W. H.) at 4 amp. per sq. in.

In order that a comparison may be made, a separate curve sheet (Fig. 2) shows the energy efficiencies of this new type of cell, and also the efficiencies of another make of cell which, so far as the author knows, is the nearest in point of view of efficiency, when compared on a basis of current density per square inch of projected electrode area.

This new type of cell, an illustration of which is shown in Fig.

3, possesses not only great flexibility of operating range and conditions for any given design, but the design itself can be adapted to widely varying circumstances such as the cost of electrical energy, which may vary considerably in different localities, and also such as the number of hours per day during which the cells are to be operated. One user may desire to run the cells 24 hours per day, while another may only desire to run them 8 hours per day, and yet another may desire to operate them at times of "off-peak," which may be somewhat intermittent.

Largely as a matter of convenience, these electrolytic cells are grouped in what is termed a "unit", such a "unit" usually comprising six cells, but the number of cells may vary from 2 up to 10 or more, being only limited by the convenience in handling, weight, etc.

Batteries of such "units" may be arranged according to the voltage of the direct current source of supply, which may be of any value up to 750 volts. The author knows of no particular limit to the voltage which can be used, and there does not appear to be any reason why batteries of such cells should not be connected to 2,400 volt D. C. interurban railway systems.

Fig. 4 shows a battery of twenty "units", each comprising six cells, the whole being designed to operate on a standard 240 to 260-volt D. C. supply system. The cells will carry 1,350 amp. at 3 amp. per sq. in., which is called the normal rating, but they will also carry up to 1,800 amp. at 4 amp. per sq. in., which is called the overload rating.

A brief description of these cells will be given so far as is possible without disclosure of features not yet fully protected by patent.

As stated, the cells are assembled in "units", each "unit" comprising, in the particular case illustrated, six cells, and each cell comprising an oxygen half-cell containing an anode, and a hydrogen half-cell containing a cathode, separated by a porous diaphragm of asbestos cloth. The body of the cell, or the cell casing, as it is called, is made of sheet steel pressed or formed to shape by die. Every such cell casing is identical and interchangeable, and is made with dimensions accurate within close limits. It should perhaps be made clear here that the oxygen half-cell casings are

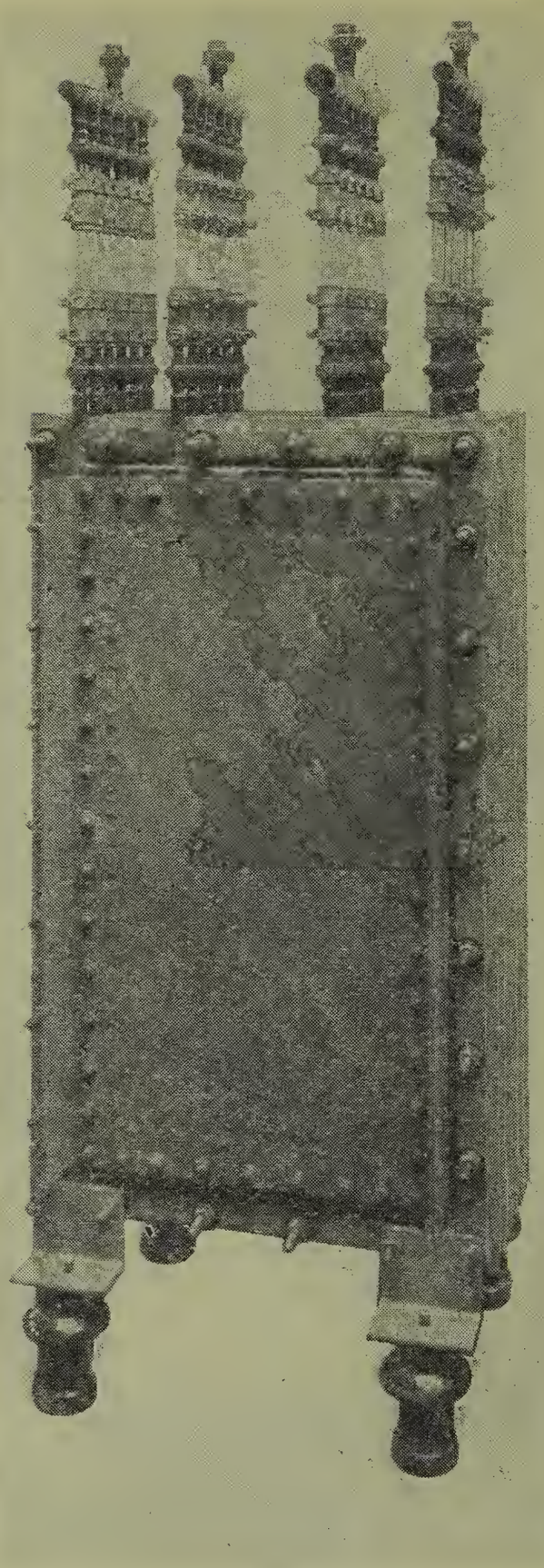


Fig. 3.

slightly different from the hydrogen half-cell casings, but this difference only consists in the size of the offtake tube. The thickness of the steel used is as light as is consistent with strength and rigidity.

The cell casings are provided with flanges so arranged that a series of such casings can be bolted together, but each and every cell casing is so arranged that the electrodes are insulated therefrom. In each six cell "unit" there is one unipolar anode, five bipolar anode-cathode pairs of electrodes, and one unipolar cathode. These electrodes are mounted on steel back supporting plates, which in turn are interleaved with the cell casings, and assembled together with suitable bolts to form the "unit" shown in the illustration (Fig. 3). The gases generated within each half-cell (termed respectively anode half-cell or cathode half-cell) are removed therefrom by way of a steel tube offtake, welded into the body ot the cell casing at the top thereof, each such offtake tube being provided with a standard union for connection to the insulating risers, and the latter being also provided with standard unions for connection to the collecting manifolds. The body of the latter is made of light steel tubing provided with steel nipples welded therein.

As these electrolytic cells are of a type wherein there is a continual circulation of electrolyte, return-flow intake tubes are also provided. These return-flow intake tubes likewise enter the cell casing at the top thereof, and are carried down inside the same to a point near the bottom. Each cell casing, representing a half-cell, has its own individual return-flow intake tube, welded into the body of the cell casing and provided with a standard union at its upper end, which is connected to a distributing manifold by risers similar to those provided on the offtakes.

From this brief description and by reference to the illustration (Fig. 3) it will be seen that at the top of each unit there are 4 manifolds, one being an offtake collecting hydrogen manifold, one an offtake collecting oxygen manifold, one a return-flow distributing manifold supplying six anode half-cells, and one a return-flow distributing manifold supplying six cathode half-cells. Each manifold is connected to the respective offtake or return-flow tubes on six half-cells by means of the glass insulating tube sections (with union at each end) shown in the illustration (Fig. 3), which latter also provide means for observing the action of the cells. The flow of electrolyte, substantially free from gas, is downwards in the two outside sets—each of six tubes—while the

flow of electrolyte, carried by and bearing gas, is upwards in the two inner sets—each of six tubes—all as shown.

The arrangement whereby all offtake and return-flow means for electrolyte and gas are kept at the top of the unit possesses considerable practical advantages, in as much as these are all readily accessible. They are under a less head or pressure of liquid than if placed at the bottom, and they are less likely to be damaged than if placed at or near the bottom, as for example when the

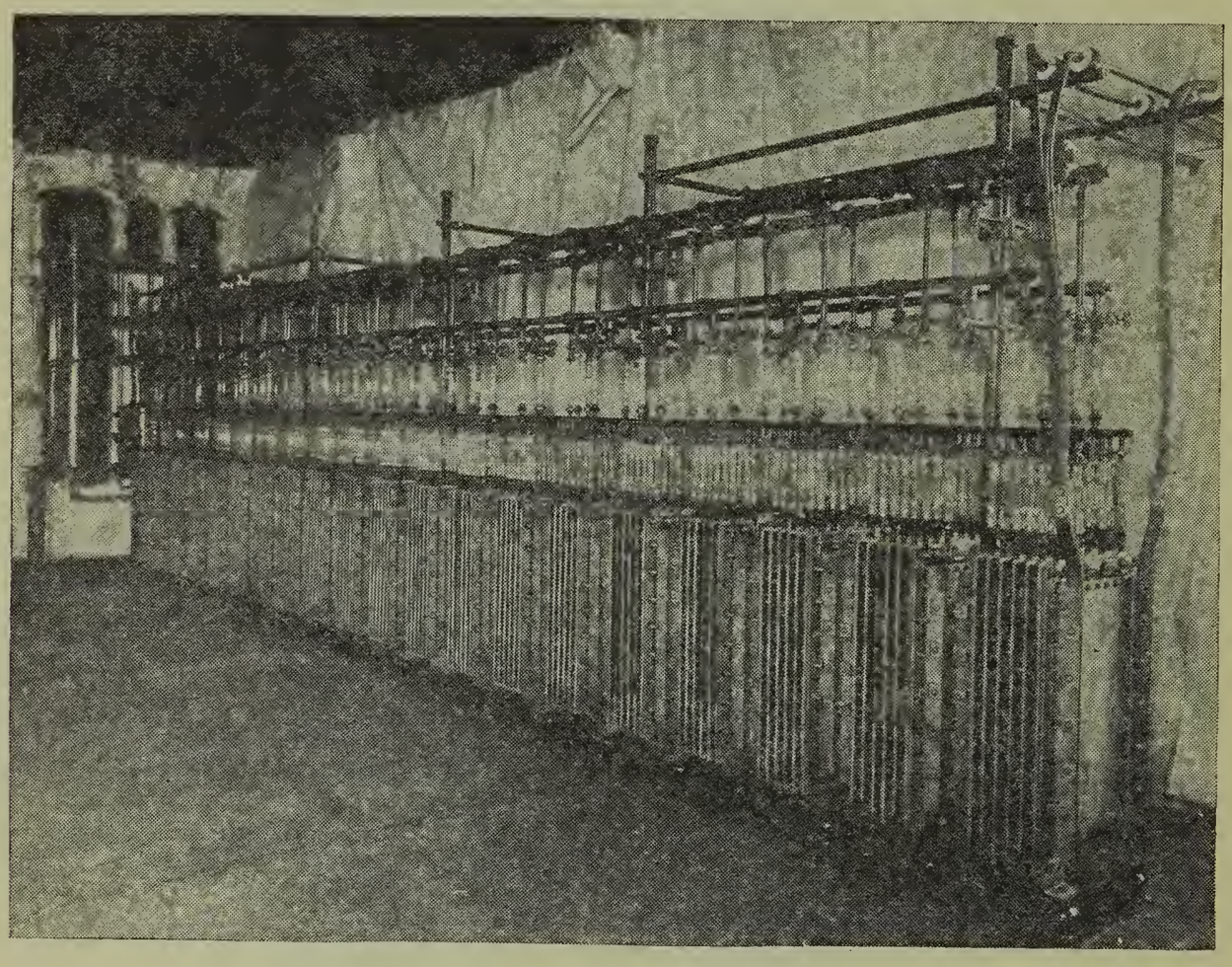


Fig. 4.

"unit" is being moved. Moreover, if any insulating tube or manifold has to be replaced or renewed, tightened up, or otherwise dealt with, it is obviously much more convenient to have them at the top.

The internal construction of the unit is such that any electrode can be replaced with a minimum of trouble, and all electrodes are uniform and interchangeable. The two unipolar electrodes are placed on the outside of the "unit". They are called "unipolar" because they carry only one electrode of one kind, either an anode

or a cathode, and as such they form the terminals of the "unit", at one of which the current enters and at the other of which the current leaves. The five bipolar electrodes are not visible in the illustration, but they are placed so that the current flows serially from one to another in its path through the "unit."

A number of such six-cell units can be placed, and connected up, in series to form a battery of cells, the number provided varying according to the voltage of the supply to which the battery is connected. Such a battery consisting of 20 units—120 cells—is shown in the illustration (Fig. 4), and it will be noticed that the unipolar electrode of one "unit" is connected to the adjacent unipolar electrode of the next unit by means of copper links which can be readily and easily disconnected if it is desired to remove the "unit" for any purpose. If a spare "unit" is available it can be placed in position instead of the one removed and connected up by the links. If a spare unit is not available, longer links can be used to bridge the gap.

The manifolds of each "unit" are connected by insulating tubes or risers, provided with standard unions on each end, to main headers, shown in the illustration, and these main headers in turn connect to the end-tanks shown in the illustration at the far end of the battery. The function of the end-tanks is to provide means for separating the gases and electrolyte, the former being taken off at or towards the top of the tank or tanks, while the latter is returned to the cells by way of the main return-flow headers. The whole action of the assembled battery is automatic as far as the flow of electrolyte is concerned. There is a continual supply of un-electrolyzed electrolyte to the lower side of the electrodes within the cells and a continual delivery of electrolyte and gas to the end-tanks where separation takes place.

In the case of the particular cell shown, the electrode measures 30 in. by 15 in., and hence has a projected area of 450 sq. in., but the actual electrolyzing area may be from 8 to 15 times as great according to the particular details of construction adopted. The whole cell is so designed that it has a very high conductivity, hence a high current carrying capacity, considering its dimensions; that is to say both its height and its width as well as its depth.

It will be observed from the illustrations that each "unit" is

supported from the floor by 4 porcelain insulators which afford ample insulation to ground. In like manner at all points of support, suitable insulation is provided, so that all current carrying parts are insulated from ground. The particular battery shown is designed to operate on a 240-volt 3-wire system, so that each end of the battery is 120 volts above ground.

The equipment is provided with separate gas washing and cooling means and pressure regulating means, the latter having an adjustable feature permitting regulation of the pressure from an equivalent of say 3 up to 12 inches of water or more as desired. There is also a combination pressure and vacuum system for use in filling and emptying the cells, and for handling the electrolyte generally. The latter being caustic potash (aqueous) is very corrosive but can be handled with safety and expedition with the system provided.

A few words may be said about the manufacture of such cells. All parts are made to die, jig, or template and dimensions are kept within limits so that they are interchangeable. Parts which are likely to suffer through wear and tear or depreciation in general are made so as to be inexpensive and easily replaced with a minimum of time and trouble. All pipe fittings are standard wherever possible, which is practically in every case.

As a manufacturing proposition every part is designed with a view to quantity production at a minimum of cost consistent with durability and low maintenance and depreciation charges.

The outside dimensions of the cells are 40 inches high by 24 inches wide and as to floor space, a unit comprising six cells such as that shown in Fig. 3, occupies a space 24 by 18 inches or 3 sq. ft., so that each cell covers a floor space of half a square foot.

This is a much smaller floor space than that occupied by any other make of cell, especially when compared with its gas producing capacity. Table III gives the floor space, current carrying capacity, and gas producing capacity of six different makes of cells, the first being the new type under discussion. The other five makes or designs of cells are designated A, B, C, D, and E respectively.

TABLE III

Floor Space of Different Makes of Cells

Designation of make of Cell	Normal Current Carrying Capacity in Amperes	Hydrogen Gas produced per cell per hour in cu. ft.	Floor Space per Cell in square feet.	Floor Space per cu. ft. of Hydrogen in square inches
New Type	1,350	21.366	0.5	3.37
A	280	4.0	0.93	33.5
B at	400	6.33	3.0	68.2
Same Cell at..	600	9.5	3.0	45.5
C at	400	6.33	2.4	54.6
Same Cell at..	600	9.5	2.4	36.4
D at	600	9.5	1.0	15.16
Same Cell at..	800	12.66	1.0	11.37
E	1,000	15.827	3.75	34.12

Under designation "B" and "C" figures are given for both 400 and 600 amperes, as the makers state that the cells are designed to operate normally at the lower current but can, if required, be operated at the higher current. Likewise with "D" which is said to have a normal rating of 600 amperes but capable of running up to 800 amperes.

The whole battery of 120 cells (20 "units") shown in Fig. 4, is capable of producing 61,500 cu. ft. of hydrogen and 30,750 cu. ft. of oxygen per 24-hour day, when operating at its normal rated current of 1,350 amp. This whole equipment occupies a floor space of 86 sq. ft. including space between the units and also space for the gas and electrolyte separating end-tanks shown at the far end.

That an equipment of oxy-hydrogen electrolytic cells should occupy as small a floor space as possible is very desirable, on account of the saving in the first cost of buildings and also the saving in the cost of cables connecting from the distributing switchboards to the cells.

A further advantage possessed by this new type of cell is the small weight of electrolyte required. As the cells may have to be emptied and refilled from time to time, this means a saving in cost and trouble of handling, as well as a saving in the first cost of the electrolyte. Table IV gives the relative weight of electrolyte per cell for the same types and makes as shown in Table III, together with the current carrying capacity, so that the figures may be reduced to a true comparative basis.

TABLE IV

Weights of Electrolyte Per Cell and Per Cu. Ft. of Hydrogen

Designation of make of cell	Normal current carrying capacity in amperes	Hydrogen gas produced per cell per hour in cubic feet	Weight of Electrolyte in lb. per cell	Weight of Electrolyte in lb. per cu. ft. of H_2 per cell per hour
New Type	1,350	21.366	60	2.81
A	280	4.0	50	12.5
B at	400	6.33	800	126.4
Same cell at..	600	9.5	800	74.2
C at	400	6.33	275	43.4
Same cell at..	600	9.5	275	29.0
D at	600	9.5	188	19.8
Same cell at..	800	12.66	188	14.8
E	1,000	15.827	1,150	72.6

These figures will have more meaning if applied to a plant for generating 1,000,000 cu. ft. of hydrogen per 24-hour day. The total weight of electrolyte would be as given in Table V.

TABLE V.

Total Weights of Electrolyte for Plant Producing a Million Cu. Ft. of Hydrogen Per Day.

Designation of make of cell	Normal Ampere Rating	Hydrogen Gas produced per cell per hr. in cu. ft.	Number of cells required	Total Weight of Electrolyte for all cells in pounds
New Type	1,350	21,366	1,950	117,000
A	280	4.0	10,417	520,850
B at	400	6.33	6,579	5,263,200
B at	600	9.5	4,386	3,508,800
C at	400	6.33	6,579	1,809,225
C at	600	9.5	4,386	1,206,150
D at	600	9.5	4,386	824,568
D at	800	12.66	3,290	618,520
E at	1,000	15.827	2,633	3,027,950

Yet another advantage possessed by this new type of cell is its light weight. Table VI compares the weight without and with electrolyte per cell, and also for the number of cells required in a plant to produce 1,000,000 cu. ft. of hydrogen per day with the same data for other competitive makes.

TABLE VI.

Weights for a Plant Producing a Million Cu. Ft. of Hydrogen Per Day.

Designation of make of Cell	Normal Ampere Rating	Number of cells	Weight per cell without electrolyte in pounds	Weight per cell with electrolyte in pounds	Total Weight for all cells without electrolyte in pounds	Total Weight for all cells with electrolyte in pounds
* New Type	1,350	1,950	127	187	247,650	364,650
A	280	10,417	417	467	4,343,889	4,864,739
B at	400	6,579	500	775	3,289,500	5,098,725
B at	600	4,386	500	775	2,193,000	3,399,150
† C at	400	6,579	700	1,500	4,605,300	9,868,500
† C at	600	4,386	700	1,500	3,070,200	6,579,000
† D at	600	4,386	500	688	2,193,000	3,017,568
† D at	800	3,290	500	688	1,645,000	2,263,520
† E	1,000	2,633	900	2,050	2,369,700	5,397,650

*These figures for total weights do not include pipe headers, nor end-tanks, which, however, would not increase the weights by much more than about 40,000 or 50,000 lb.

†The figures of weights of these cells without electrolyte are approximate.

It will be noticed from these figures that the weight of the cells and of the electrolyte, especially in a large plant, become enormous when cells of other makes are considered, but is very much lower and more within reason with the new type of cell under discussion.

There is no reason why such heavy apparatus, nor why such enormous quantities of electrolyte, should be involved, as there are no compensating advantages. It must be clear that there are considerable disadvantages, not only as to first cost, but also as to space occupied, convenience and time taken in handling, etc.

In order to give some idea as to the floor space occupied, Table VII has been prepared, applicable to a plant capable of producing one million cu. ft. of hydrogen per day.

These figures will give some idea of the saving, in the first cost of buildings to house the plant, by the use of this new type of cell. There are also savings in maintenance costs of buildings, taxes, fire insurance, etc., all of which go towards lowering the cost of the gases and bringing them within reach of many users, whose processes require cheap hydrogen and oxygen.

In all commercial undertakings the costs of production and the selling prices or values of the products are important. The different items which enter into the cost of producing hydrogen

TABLE VII.

Floor Space Occupied by an Electrolytic Cell Plant Capable of Producing One Million Cu. Ft. H_2 Per Day.

Designation of make of cell	Normal Ampere Rating	Number of cells required	Net Floor Space per Cell in sq. ft.	Total Net Floor Space Excluding Passage ways and Space Between in sq. ft.
New Type ...	1,350	1,950	0.5	975*
A	280	10,417	0.93	9,688
B at	400	6,579	3.0	19,737
B at	600	4,386	3.0	13,158
C at	400	6,579	2.4	15,790
C at	600	4,386	2.4	10,526
D at	600	4,386	1.0	4,386
D at	800	3,290	1.0	3,290
E	1,000	2,633	3.75	9,874

*1400 sq. ft. including end-tanks and space between "units."

and oxygen gases by electrolytic process will vary according to circumstances, and their relative importance in the total cost per unit volume of the gases will depend on a number of conditions, such as the cost of the electrical energy, the rate of interest paid for money, the rate allowed for depreciation, maintenance, etc.

Enumerating the different parts of the cost of the gases, these are:

(1) The cost of the electrical energy.

(2) The fixed charges, which include:
- (a) Interest on investment.
- (b) Taxes.
- (c) Fire insurance.

(3) The depreciation, maintenance, repairs, and renewal charges.

(4) The cost of labor.

(5) The cost of water.

(6) The charges for buildings and auxiliary equipment.

The cost of the electrical energy is a very important item, and bears a degree of importance with respect to the other charges which become greater the greater the price for the electrical

energy, and *vice versa.* The discussion of this item will be dealt with later.

Taking up the matter of fixed charges, we may assume that money will cost 7 percent per annum, taxes and fire insurance may be taken at 3 percent per annum, giving a total of 10 percent per annum.

The curves in Fig. 5 show the first cost of electrolytic cells of different normal rated current-carrying capacities. The upper

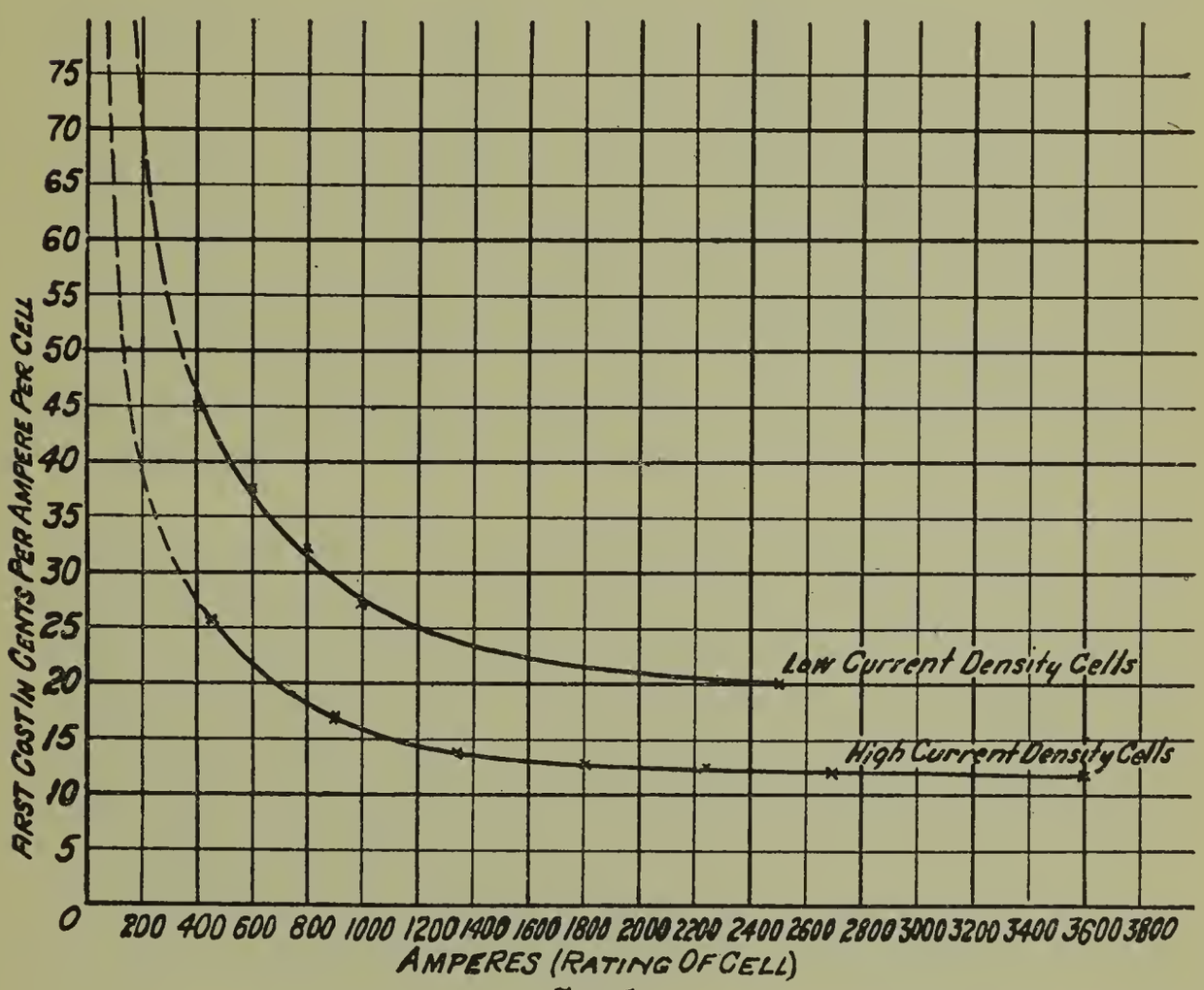


Fig. 5.

of the two curves shows the relation between the first cost expressed in cents per ampere per cell (amperes per cell being a function proportionate to gas-producing capacity) and the rated current-carrying capacity of the cell. This curve is plotted from actual prices and shows that the larger the rated current capacity, the lower the first cost of the cell, a fact which is to be expected. This curve applies only to cells which operate at low current densities, say from 0.1 to 0.5 amp. per sq. in. of projected electrode area. It will be seen that it tends to become horizontal as

the current rating of the cell is increased, and at 4,000 to 5,000 amperes the cost would be between 18 and 20 cents per ampere per cell.

The lower curve shows the same relations for high current density cells, operating at 3 amp. per sq. in. of projected electrode area. It shows that the first costs of such cells are below two-thirds of the first costs of low current density cells, which means that the material and labor embodied in the former are used to better advantage as regards gas-producing capacity. These curves also indicate that the fixed charges on high current density cells will be much lower than on low current density cells.

The next item of cost is depreciation, maintenance, etc., and will, the author presumes, form a point of criticism against the high current density cell. It will be said that working at high current density will inevitably lead to severe and rapid deterioration of the electrodes and other parts of the cells. This is not so, however, provided the design is correctly proportioned and care is taken to operate at currents and voltages at which the electrodes still retain their passivity.

In the latest designs of this new type of cell, there was no appreciable change in either the electrodes or the diaphragms after test runs for two months for an average of eight hours per day. During these runs the current density rose to 4 amp. per sq. in. (*i. e.,* 1,800 amp.), and operation was mostly always above 2 amp. per sq. in., averaging probably 3 amp. per sq. in. (*i. e.,* 1,350 amp.)

Until experience has been gained over a period of a number of years of actual operation, it is not possible to say exactly what would be the correct rate for depreciation to be taken for any particular current density. As it is desirable to have an estimate of depreciation, in order to arrive at the cost of the gases under any series of given conditions, we may take it that the rate for depreciation will vary as a function of the current density, and to ascertain the influence on the cost of the gases of different rates of depreciation for the same current density, the author has determined these rates for depreciation as made to vary in three different functions of the current density, first, as the square root; second, as the three-fourth power; and third, as the first power, which is in direct proportion to the current density. These rates are give in Table VIII.

TABLE VIII.

Percentages for Depreciation, Etc., Under Three Different Variable Functions.

Current Density amp. per sq. in.	Function as square root. Percent	Function as ¾th power. Percent	Function in direct Proportion. Percent
0.5	1.77	1.49	1.25
1	2.5	2.5	2.5
1.5	3.06	3.4	3.75
2	3.54	4.2	5
2.5	3.95	4.97	6.25
3	4.33	5.7	7.5
3.5	4.67	6.4	8.75
4	5	7.1	10

This table has been used in later calculations of the costs of the gases per million cu. ft. per day. The three columns of percentages represent the minimum, the mean, and the maximum respectively.

The cost of labor is a relatively small part of the total cost of the gases, and this is especially the case in a large plant. It will, roughly speaking, be greater the larger the number of cells, as one man will only be able to attend satisfactorily to a limited number of cells. If the cells are operated at low current density, there will be more cells, while at high current density there will be fewer cells for a given gas output. In such case the cost would vary inversely as the current density.

However, no hard and fast rules can be laid down and each design of cell must be considered, as far as the cost of operating labor is concerned, separately and according to experience gained.

The hydrogen and oxygen gases are obtained by the electrolytic decomposition of water, which may be considered as the raw material of the process. While water is cheap, it nevertheless costs something, especially if it has to be distilled in order to purify it.

In this connection, it is worth while mentioning that it is not advisable to use water in electrolytic cells which contains impurities, not only on account of possible corrosive action on the electrodes, but also because certain impurities are likely to be

precipitated in the cell or in some part of the electrolyte circulating system, and, collecting there, will ultimately block up some vital point. Certain impurities in the water might also be harmful to the diaphragms, which are more or less sensitive to collections of sedimentary deposits.

The cost of the distilled water may be taken at half a cent per gallon, and one gallon (U. S. Std.) will yield 178.26 cu. ft. of hydrogen and approximately half this volume of oxygen, both measured at 20° C. and 760 mm. pressure.

TABLE IX.

Current and Voltage Per Cell.

Current Density in Amp. per sq. in.	Volts per Cell	Percent Energy Efficiency	Cu. ft. of Hydrogen per K. W. H.	Cu. Ft. of Oxygen per K. W. H.
0.1	1.75	85.50	9.045	4.523
0.2	1.83	81.75	8.66	4.33
0.3	1.90	78.74	8.33	4.17
0.4	1.96	76.32	8.07	4.04
0.5	2.00	74.80	7.91	3.96
0.6	2.025	73.88	7.82	3.91
0.7	2.045	73.15	7.74	3.87
0.8	2.06	72.60	7.68	3.84
0.9	2.07	72.28	7.64	3.82
1.0	2.08	71.92	7.61	3.805
1.5	2.15	69.58	7.36	3.68
2.0	2.22	67.39	7.13	3.565
2.5	2.27	65.90	6.912	3.486
3.0	2.32	64.48	6.822	3.411
3.5	2.36	63.39	6.70	3.35
4.0	2.40	62.33	6.594	3.297

The author considers that the best way to take account of the various charges for buildings, etc., at least for the purposes of this paper, is to take this as a rental on the floor space, which will cover fixed charges, depreciation, maintenance, taxes, and insurance. Such floor space should be available at 50 cents per sq. ft. per annum.

The question of the energy used by this new type of electrolytic oxy-hydrogen cell may now be taken up. The curves in Figs. 1 and 2 show the efficiencies of this cell at different current densities. The exact figures of current and voltage per cell are

repeated in Table IX for the sake of greater clearness, and from these figures the energy required may be calculated for any size of cell and for any size of plant.

Table IX does not give the actual current flowing through the cells, but only the current density per sq. in. of projected electrode area. The convenience of this is that the table may be applied to a cell of any desired size. For example, it has been proposed to have a standard line of cells whose electrodes will have the projected area ranging in steps of 150 sq. in., beginning with an electrode 30 by 10 inches = 300 sq. in., the height (30) being kept constant, while the width varies in steps of 5 in. Thus a series of standard cells such as indicated in Table X are developed.

TABLE X.

Standard Cells (New Type).

Size of Electrode Inches	Area of Electrode in sq. in.	Normal Maximum Current Amp.	Overload Current Amp.	Cu. Ft. of Hydrogen per cell per hour		Kilowatts per Cell	
				At Norm. Maximum	At Overload	At Norm. Maximum	At Overload
30 x 10	300	900	1,200	14 244	18.992	2.088	2.88
30 x 15	450	1,350	1,800	21.366	28.488	3.132	4.32
30 x 20	600	1,800	2,400	24.488	37.984	4.176	5.76
30 x 25	750	2,250	2,800	35.610	47.480	5.220	6.72
30 x 30	900	2,700	3,600	42.732	56.976	6.264	8.64
40 x 30	1 200	3,600	4,800	56.976	75.968	8.352	11.52
50 x 30	1,500	4,500	6,000	71.220	94.960	10.440	14.40

The seventh and eighth columns in Table X give the power taken, and from these figures the daily cost of energy may be obtained. Likewise, columns 5 and 6 give the volume of hydrogen per cell, from which the cost per unit volume may be arrived at by a simple calculation. The volume of oxygen per cell is, of course, approximately half the volume of the hydrogen.

Having dealt briefly with the six items entering into the cost of producing hydrogen and oxygen by the electrolytic decomposition of water, the author will proceed to show the influence of current density measured in amperes per sq. in. of projected electrode area, and for this purpose has prepared a series of tables and curves.

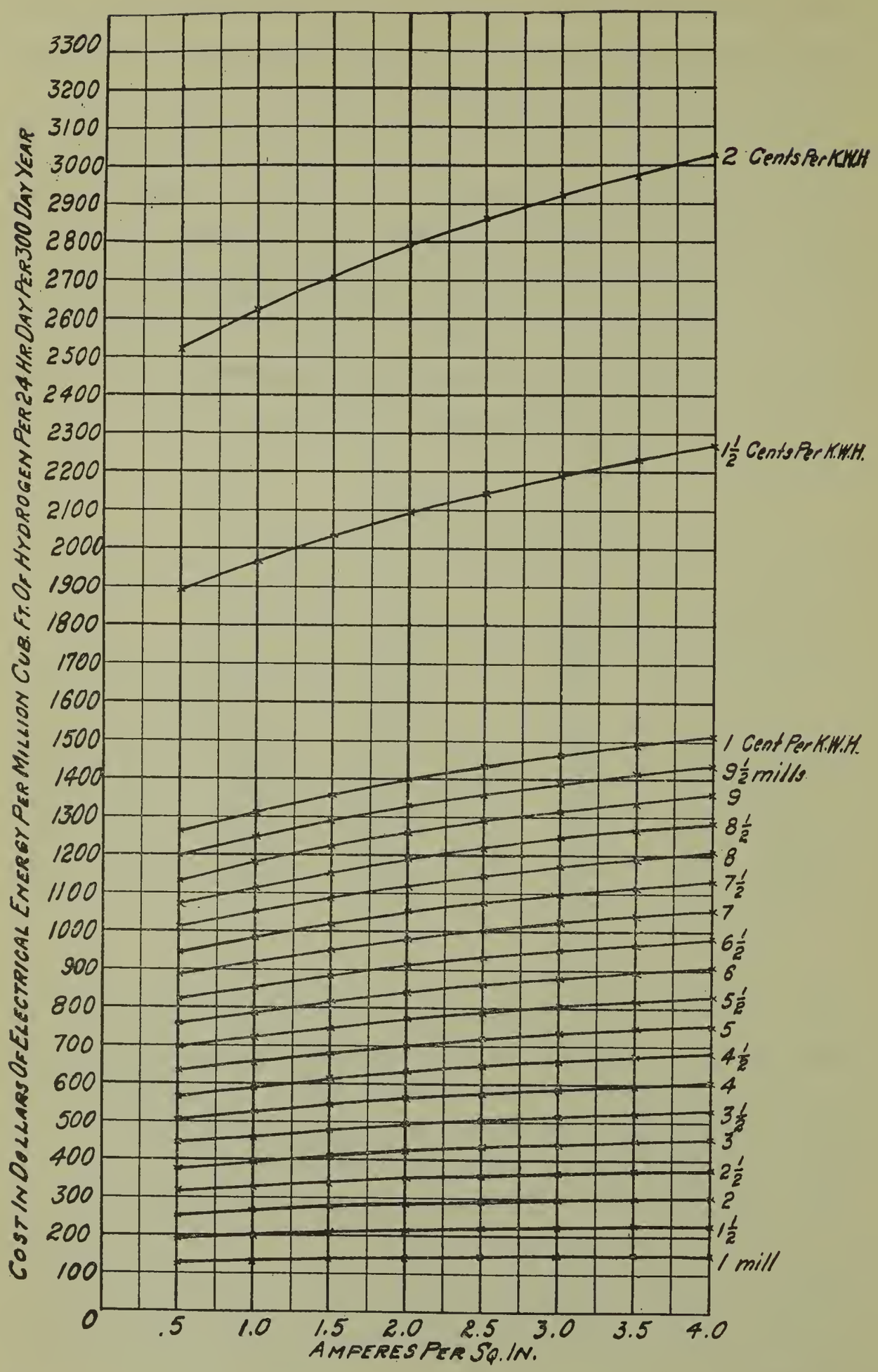

Cost In Dollars Of Electrical Energy Per Million Cub. Ft. Of Hydrogen Per 24 Hr. Day Per 300 Day Year
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Amperes Per Sq. In.
2 Cents Per K.W.H.
1½ Cents Per K.W.H.
1 Cent Per K.W.H.
9½ mills
9
8½
8
7½
7
6½
6
5½
5
4½
4
3½
3
2½
2
1½
1 mill

Fig. 6.

By way of preliminary explanation, it may be said that the case of a plant capable of generating 1,000,000 cu. ft. of hydrogen per 24-hour day and, of course, half this volume of oxygen, has been taken, and all curves are plotted with dollars as ordinates and current density per sq. in. of projected electrode area as abscissæ.

In order to deal with round figures as much as possible, the plant has been assumed to consist of such a number of cells that when this number is multiplied by the current density in amperes per sq. in., the product is 3,000 amp.-cells. The projected area of the electrode is taken at 875 sq. in. and Table XI is constructed for current densities from 0.5 to 4 amp. per sq. in. The first cost of each cell in the plant is assumed at $200.

TABLE XI.

Data for Plant Producing Million Cu. Ft. of Hydrogen Per Day.

Current Density in Amperes per sq. in.	Number of Cells	Cost per Cell	Total Cost of all Cells	Voltage per Cell in Volts	Current per Cell in Amp.	K. W. H. per 24-hr. Day
0.5	6,000	$200.	$1,200,000	2.0	437.5	126,000
1	3,000	"	600,000	2.08	875	131,040
1.5	2,000	"	400,000	2.15	1,312.5	135,450
2	1,500	"	300,000	2.22	1,750	139,860
2.5	1,200	"	240,000	2.27	2,187.5	143,010
3	1,000	"	200,000	2.32	2,625	146,160
3.5	856	"	171,200	2.36	3,062.5	148,482
4	750	"	150,000	2.40	3,500	151,200

From the seventh column, it is possible to obtain the cost of the electrical energy required to produce one million cu. ft. of hydrogen per day, and this cost may be readily calculated for different rates for power from, say, one mill to two cents per K. W. H. This has been done and the results plotted in a series of curves in Fig. 6.

It will be noticed from these curves that at the lower rates for power, they are much flatter than at the higher rates. This indicates that, for cheap power, operation at high current densities with consequent sacrifice—to at least some degree—of energy efficiency, does not burden the total costs of the hydrogen with a great increase, because of the increased cost of the necessary electrical energy, and it will be shown in what follows that any

such increase is offset by the decrease in the costs of the remaining five items.

Taking up the fixed charges next, these have been calculated for 300 working days per year at the rate of 10 percent per annum. They vary inversely as the current density, as will be seen from Table XII.

TABLE XII.

Fixed Charges at 10 Percent Per Annum for a 300-Day Year for Plant Producing Million Cu. Ft. of H_2 Per Day.

Current Density in Amp. per sq. in.	Number of Cells	Total Cost of All Cells	Daily Cost of Fixed Charges
0.5	6,000	$1,200,000	$400.00
1	3,000	600,000	200.00
1.5	2,000	400,000	133.33
2	1,500	300,000	100.00
2.5	1,200	240,000	80.00
3	1,000	200,000	66.66
3.5	856	171,200	57.11
4	750	150,000	50.00

The depreciation charges have been calculated from the table of percentages, Table VIII, and the figures on each of the three bases are given in Table XIII. The figures in columns 2, 3 and 4 give the daily costs based on a 300-working-day year. They are embodied in the curves of total costs per million cu. ft. of hydrogen.

TABLE XIII.

Depreciation Charges for a 300-Day Year for a Plant Producing a Million Cu. Ft. of H_2 Per Day.

Current Density in Amp. per sq. in.	Daily Depreciation Charges		
	Minimum Basis	Mean Basis	Maximum Basis
0.5	$70.80	$59.60	$50.00
1	50.00	50.00	50.00
1.5	40.80	45.33	50.00
2	35.40	42.00	50.00
2.5	31.60	39.76	50.00
3	28.87	39.00	50.00
3.5	26.67	36.55	50.00
4	25.00	35.50	50.00

The figures for the last three items in the total cost are given in Table XIV.

TABLE XIV.

Labor, Water, and Rental Charges for a 300-Day Year for a Plant Producing a Million Cu. Ft. of H_2 Per Day.

Current Density in Amp. per sq. in.	Daily Labor Charges	Daily Charges for Distilled Water	Daily Charges for rental of Floor Space
0.5	$192.00	$28.05	$40.00
1	96.00	28.05	20.00
1.5	64.00	28.05	13.33
2	48.00	28.05	10.00
2.5	38.40	28.05	8.00
3	32.00	28.05	6.66
3.5	27.40	28.05	5.71
4	24.00	28.05	5.00

The figures for the cost of distilled water are derived as follows:

Water to generate 1,000,000 cu. ft. of Hydrogen =

$$\frac{1{,}000{,}000}{178.26} = 5{,}610 \text{ U. S. gallons.}$$

The cost of this water purified by distillation is taken at 0.5 cent per gallon.

Using the figures in Tables XI to XIV in conjunction with the curves as per Fig. 6, three series of curves are obtained as per Figs. 7, 8, and 9, giving the total costs of hydrogen per million cu. ft.

Fig. 7 curves embody the minimum rates for depreciation, etc.; Fig. 8 curves, the mean rates for depreciation, etc., and Fig. 9 the maximum rates for depreciation, etc.

An examination of these curves discloses the fact that the total costs of the gases per unit volume are a maximum at half an ampere per square inch current density, even at rates for power up to 2 cents per K. W. H. The total costs drop rapidly with increasing current density, and reach a minimum at current densities which vary according to the cost of power. Beyond these current densities the total costs increase, but on a curve which is not nearly so steep. The dotted line is the locus of the points of

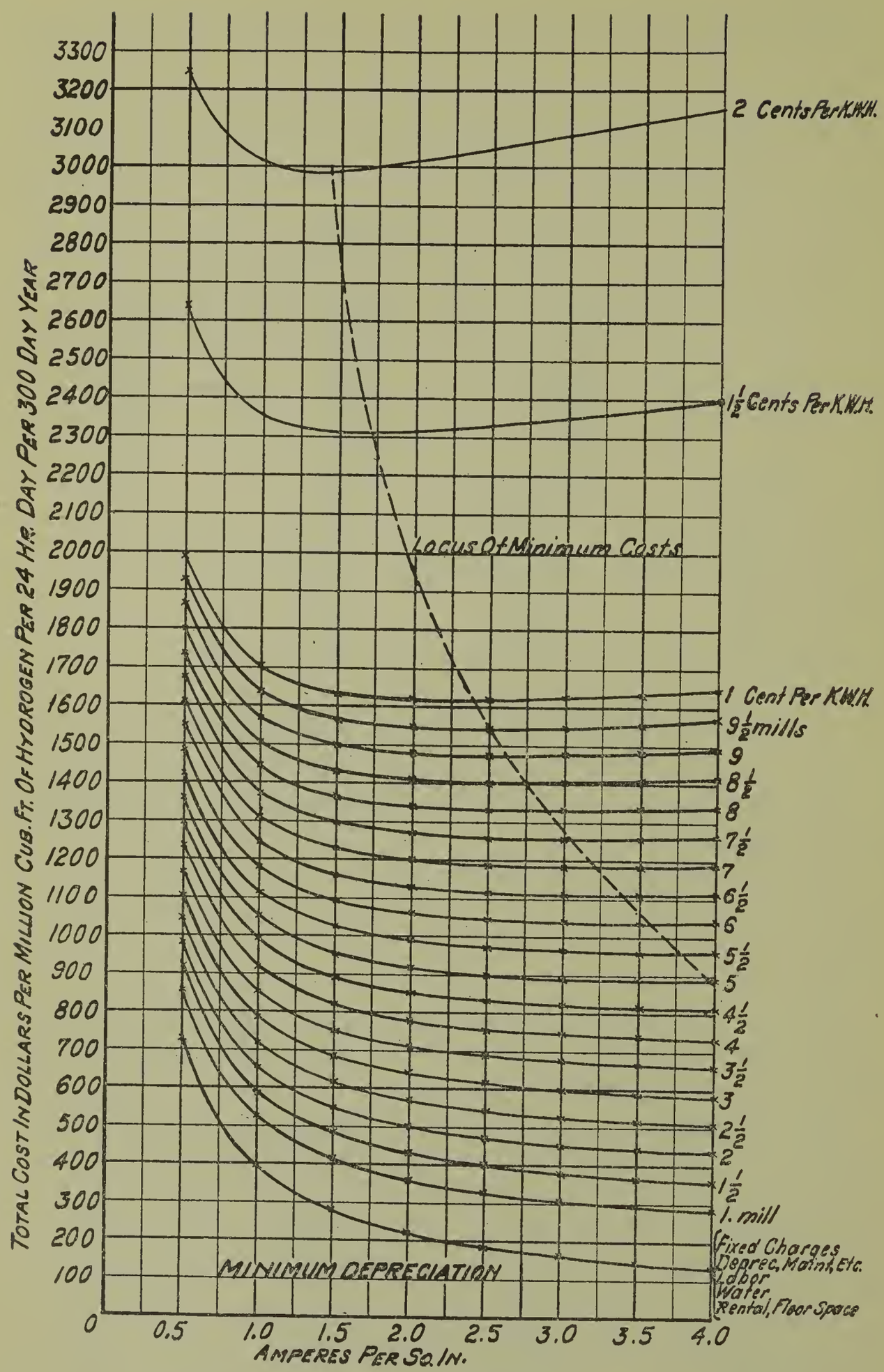

Total Cost In Dollars Per Million Cub. Ft. Of Hydrogen Per 24 Hr. Day Per 300 Day Year
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Amperes Per Sq. In.
2 Cents Per K.W.H.
1½ Cents Per K.W.H.
Locus Of Minimum Costs
1 Cent Per K.W.H.
9½ mills
9
8½
8
7½
7
6½
6
5½
5
4½
4
3½
3
2½
2
1½
1. mill
Fixed Charges
Deprec. Maint. Etc.
Labor
Water
Rental, Floor Space
MINIMUM DEPRECIATION

Fig. 7.

minimum total costs. This locus shows that the point of minimum costs gradually moves forward from about 1.37 amp. per sq. in. current density when power costs 2 cents per K. W. H., and the maximum rate for depreciation is taken, until it disappears in the direction of current densities still higher than 4 amp. per sq. in. when power costs 4 mills per K. W. H. and the maximum depreciation rate still applies.

The locus has been drawn in on all three sets of curves, Figs. 7 to 9, and if one set of curves could be placed on top of the other, it would be seen that the locus line for the mean rate of depreciation is slightly in advance—that is, in the direction of higher current densities—of the locus line for the maximum rate for depreciation. Likewise, the locus line for the minimum rate for depreciation is slightly in advance of both the other two locus lines. The difference in position of all three locus lines is not great, however, thus showing that the influence of depreciation is not so great as might be thought.

The foregoing discussion, it will be understood, applies to a type of cell having the efficiency characteristics of Fig. 1. It does not apply to a given installation, in which the number of cells, and the current density at which operation will be carried on, have already been determined. A definite installation of a fixed number of cells and a predetermined current density of operation would require rather a different method of treatment.

The curves in Figs. 7, 8, and 9, however, give, at a glance, the cost of producing hydrogen and oxygen per million cubic feet per 24-hour day, based on 300 working days in a year. The most economical current density at which to operate is also indicated if the cost of the electrical energy is known.

The electrical power plants of the United States and Canada, particularly the hydro-electric plants, have a large surplus of generating power available for several hours each day, so-called "off-peak" power. The fixed charges for this plant are running whether the plant is being operated or is lying idle awaiting a demand. The added cost of operating the surplus generating plant at times of "off-peak" will be comparatively small. Such added costs will be a small amount to cover additional operators, lubrication, wear and tear of machines, and possibly something for

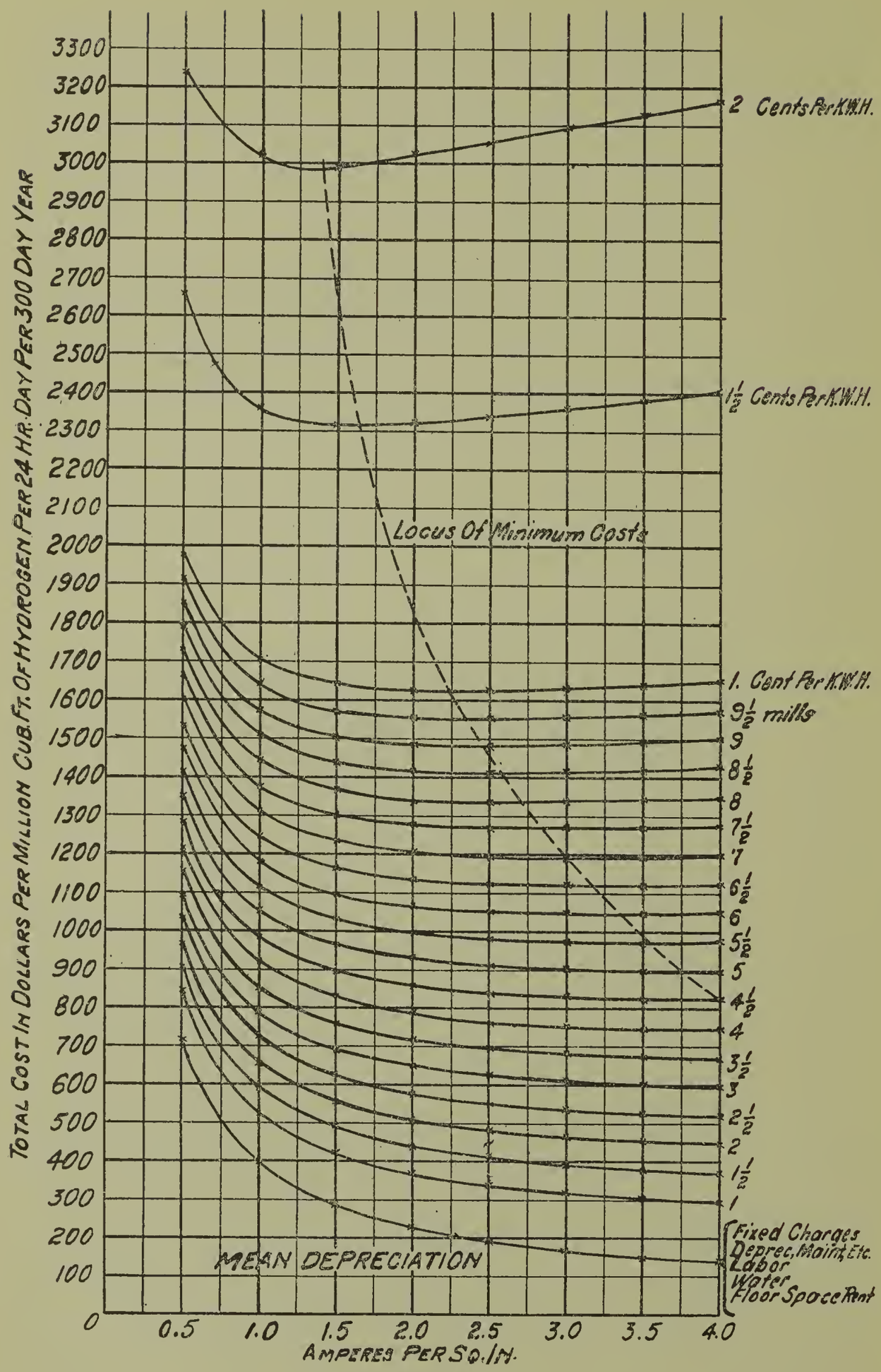

TOTAL COST IN DOLLARS PER MILLION CUB. FT. OF HYDROGEN PER 24 HR. DAY PER 300 DAY YEAR
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
AMPERES PER SQ. IN.
2 Cents Per K.W.H.
1½ Cents Per K.W.H.
Locus Of Minimum Costs
1. Cent Per K.W.H.
9½ mills
9
8½
8
7½
7
6½
6
5½
5
4½
4
3½
3
2½
2
1½
1
MEAN DEPRECIATION
Fixed Charges
Deprec. Maint. Etc.
Labor
Water
Floor Space Rent

FIG. 8.

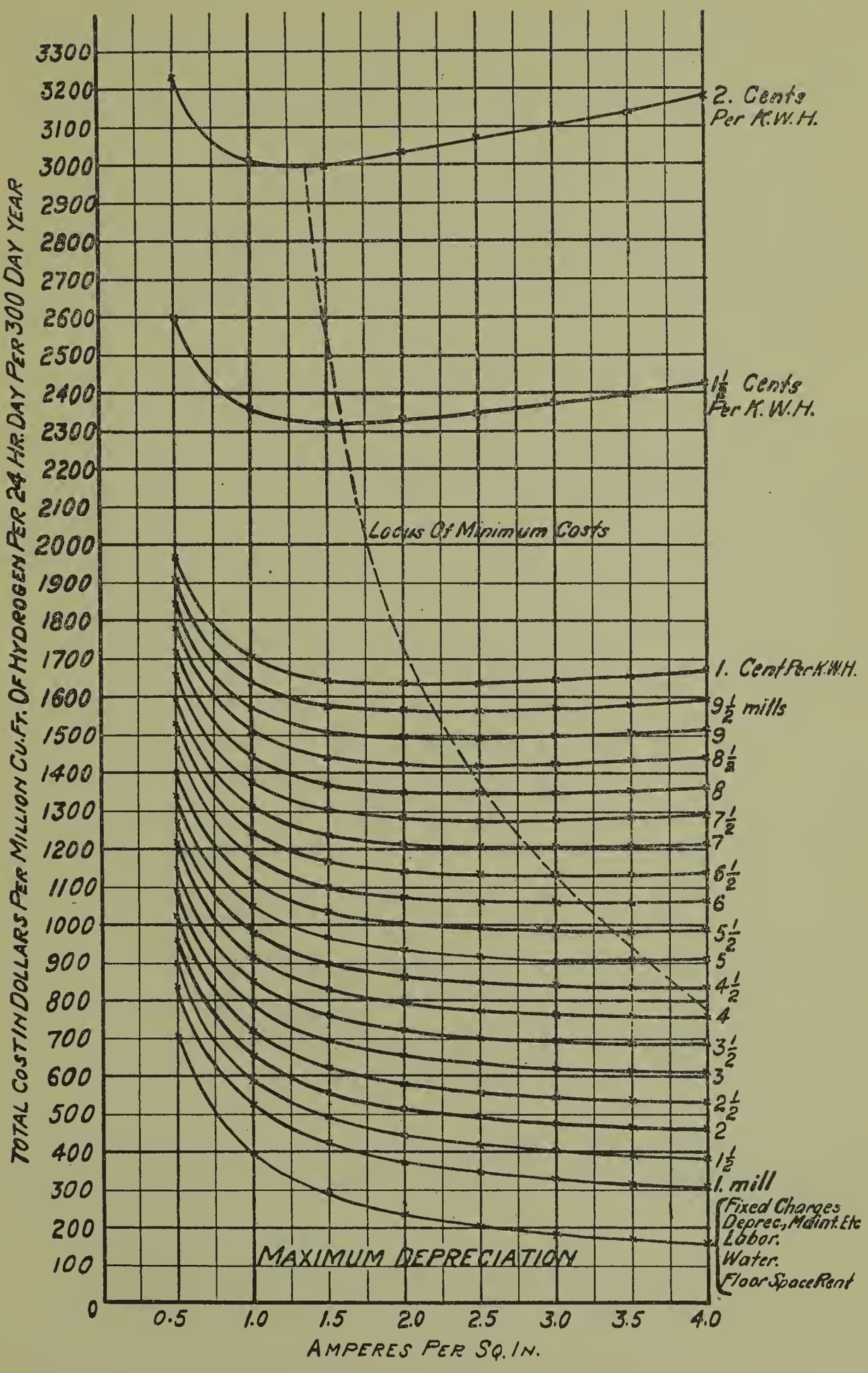

TOTAL COST IN DOLLARS PER MILLION CU. FT. OF HYDROGEN PER 24 HR. DAY PER 300 DAY YEAR
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
AMPERES PER SQ. IN.
2. Cents Per K.W.H.
1½ Cents Per K.W.H.
Locus Of Minimum Costs
1. Cent Per K.W.H.
9½ mills
9
8½
8
7½
7
6½
6
5½
5
4½
4
3½
3
2½
2
1½
1. mill
Fixed Charges
Deprec., Maint. Etc
Labor.
Water.
Floor Space Rent
MAXIMUM DEPRECIATION

FIG. 9.

extra depreciation. The fixed charges may be considered as wholly covered by the normal demand. Thus it is conceivable that "off-peak" power could be sold for as low as one mill per K. W. H. and probably would not exceed 2.5 mills per K. W. H. under the most unfavorable conditions.

A reference to the universal cost curves, Fig. 9, (maximum rate for depreciation), will show that, at 3 amperes per square inch, a daily output of one million cubic feet of hydrogen and half this volume of oxygen can be obtained for $330 with 1-mill power, or for $546 with 2.5 mill power.

If both gases are used in their entirety and given an equal value, they will cost, in the former case, 22 cents per 1,000 cu. ft., and, in the latter case, 36.4 cents per 1,000 cu. ft. Even if all the oxygen were discarded or at least given no value at all, the hydrogen would have cost only 33 cents per 1,000 cu. ft., in the former case, and 54.6 cents per 1,000 cu. ft. in the latter case. On the other hand, if all the hydrogen were discarded or given no value at all, the oxygen would have cost only 66 cents per 1,000 cu. ft. in the former case, and $1.092 per 1,000 cu. ft. in the latter case.

Again, the cost of production may be shared in any proportion between the two gases, according to the market value of either. For example, if the market for the hydrogen warranted that it bear a cost charge of 30 cents per 1,000 with power at 1 mill per K. W. H., then this leaves only 6 cents per 1,000 to be borne by the half million cubic feet of oxygen, which is equal to $1.50 per ton of oxygen, and many processes could be carried out economically at this figure. Once the possibility of obtaining cheap hydrogen and oxygen is conceded, the outlook for their use widens indefinitely, and with cheap cost of production we may be enabled to make remarkable and hitherto unthought of advances in arts and manufacture.

A few present uses for the gases and some suggestions for future possibilities are given hereunder and no doubt there are many others.

Present Uses of Hydrogen

Hydrogen gas has been and can be used for the following purposes:—

(1) Obtaining high temperatures from the heat energy given

out when hydrogen and air or oxygen are burned in a suitable torch, furnace or cupola.

(2) The hydrogenation of oils and other unsaturated fatty acids.

(3) The synthetic production of ammonia.

(4) As an inert (or reducing) atmosphere in certain manufactures such as the process of making tungsten filament lamps, annealing of steels, and general treatment of metals at high temperatures.

(5) The filling of balloon or air-ship gas bags.

(6) The calorizing of iron or steel tubes.

(7) The reduction of tungsten, molybdenum, and other ores.

(8) The melting of metals which have a relatively high melting point, and where a clean, pure, non-oxidizing atmosphere is desirable, such as in the case of the precious metals.

(9) The melting and working of glasses of different kinds; also quartz, and silica ware of various kinds.

(10) The making of glass thread and from that of glass cloth.

(11) The manufacture of artificial or imitation precious stones, which are made of colored quartz.

Many possible future uses might be suggested and new ones are coming to light from time to time. We might name the following:

(a) The cracking of oils with the production of various hydro-carbons, gaseous or liquid, the reaction to be carried out in a hydrogen atmosphere.

(b) The increase of the calorific power of coal gas by the use of hydrogen to make methane (CH_4), or other hydro-carbons of higher heat value.

(c) The increase of the illuminating power of coal gas by the use of hydrogen to make ethylene (C_2H_4) or other hydro-carbons of higher illuminating power.

(d) Obtaining a supply of nitrogen by burning out the oxygen in air with hydrogen.

(e) The burning of hydrogen and oxygen to raise steam or the utilization of the steam and hot nitrogen in (d) to drive low

pressure turbines and thus recover part of the available energy, which would otherwise be lost in condensation, when the steam was separated as water from the nitrogen.

Present Uses of Oxygen

(1) For obtaining high temperatures generally by using pure oxygen instead of air, as for instance in the oxy-hydrogen or oxy-acetylene blow-pipe or torch.

(2) For medicinal purposes, such as destroying bacteria, artificial respiration, etc.

(3) For use in assisting the recovery of persons overcome by noxious fumes or gases.

(4) For burning out carbon or soot in internal combustion engines, flues, chimneys, etc.

(5) For use with hydrogen in all cases previously enumerated where high temperatures are required.

As to possible future uses, reference might be made to the suggestions of the late J. E. Johnson, Jr., in Met. and Chem. Eng., 1915, **13,** 483, where he examines the possibility of using oxygen or enriched air for the blast in the reduction of iron ores in the blast furnace, thus enabling ores of much lower iron content to be commercially and profitably handled.

This leads directly to the suggestion of the possibility of using oxygen, or air enriched with oxygen, in many processes involving reactions with carbon where high temperatures are essential to produce the reaction and which at present use the electric furnace, as for example, in the manufacture of calcium carbide, the manufacture of water gas, and from this latter, if desired, making more hydrogen.

It has also been suggested that oxygen, if cheap enough, might be piped and delivered as illuminating gas is at present, and in such cases the oxygen could be used as a richer and enclosed atmosphere, within which to burn coal gas with gas mantles, thus obtaining very high illuminating power and intense lights of greater efficiency.

Oxygen might also be used for the manufacture of sulphur-trioxide, SO_3, from sulphur-dioxide, SO_2, in the chamber or contact processes of making sulphuric acid.

Many of the possible uses for these two gases would be and are dependent on an abundant supply at low cost, and by the latter is meant, say, under 50 to 75 cents per 1,000 cu. ft. for hydrogen and under, say, $1.00 per 1,000 cu. ft. for oxygen.

Using oxygen to make or assist in carrying out the process of making sulphuric acid, and using hydrogen to make ammonia, we can obtain from the ammonia and the sulphuric acid, ammonium sulphate, which constitutes one of, if not the most important, chemical manure or fertilizer known to man. During the year 1916, 350,000 tons of ammonium sulphate were produced in Great Britain, the larger part of which was consumed in agriculture.

Using oxygen or enriched air in the manufacture of nitrogen dioxide in the arc process, and also for the ultimate absorption of the nitrogen dioxide by water, to produce nitric acid.

Using oxygen or enriched air for the oxidation of ammonia to nitric acid. This is referred to by W. S. Landis in the Proceedings of the American Electrochemical Society, 1919, **35,** 283.

DISCUSSION.

Carl Hering[1]: Were any measurements made to possibly increase the electrical efficiency by increasing or decreasing the atmospheric pressure in the cells? In a paper I read before this Society (An Electrochemical Paradox. Trans. 1902, **2**, 139) I described an experiment in which visible decomposition took place at about 0.3 volt when the pressure was increased to about 14 atmospheres. It is probable however that less gases were produced then than would correspond to Faraday's law. It may perhaps not yet be definitely settled whether the physical energy consumed in changing the liquid into gas comes from the electric circuit or not. If liquid oxygen and hydrogen were vaporized under water this latent heat of vaporization would surely be taken from the heat of the water.

Colin G. Fink[2]: I was very much interested in this paper, and particularly so in the list of uses for hydrogen. Under No. 7 is

[1] Consulting Electrical Engineer, Philadelphia, Pa.
[2] Consulting Electrometallurgist, New York City.

the reduction of ores. Now that may seem rather strange to some of you that it really will pay to reduce metallic ores by hydrogen, but we have carried out a long series of experiments, and were surprised at the low cost figures. The high price of hydrogen is more than offset by the very low temperature of operation, the comparative absence of slagging materials and the very simple furnace construction.

V. T. STEWART[3] (*Communicated*): The commercial usefulness of hydrogen is greatly hampered by its outstanding property, namely, being the lightest known substance. Hydrogen therefore becomes what the economists call a place utility. It must be used, if on any appreciable scale, near its point of origin. It is further curtailed by the fact that for many uses, the gas must be in the nascent form.

Hydrogen is used on an extensive scale for the hydrogenation of oils for food, soap, and other purposes, for the synthetic manufacture of ammonia, and for aviation. For all of these purposes, it is usual to have a hydrogen plant adapted to the special needs of each situation.

The smaller scale commercial uses of hydrogen are limitless. Those which use the element in the nascent form will be passed over here.

One would expect that the chlorine-caustic soda cell would be a large producer of by-product hydrogen. However the difficulties of collection and purification, together with the restrictions noted above, have so definitely circumscribed this source that there is little or no use made of the gas. A few plants here and there make some attempt to utilize the gas for some of the purposes mentioned herewith.

For certain metallurgical operations, hydrogen has the advantage of inertness, or a reducing atmosphere. In the annealing of ingot iron, the presence of an atmosphere of hydrogen modifies the properties of the metal enormously. Steel is prepared for nickel plating by heating and cooling in such an atmosphere. In both of these cases, the prevention of oxidation and the thorough reduction of all parts are of more than apparent usefulness.

[3] Montclair, N. J.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

THE PRODUCTION OF HYDROGEN BY THE USE OF SILICON AND SODIUM HYDROXIDE

By E. R. Weaver.[2]

Abstract.

The author describes the generation of hydrogen by the "silicol" process, which has been found very adaptable for military and naval use. The non-combustibility of the materials used insures safety of transportation. The rate of reaction of ferrosilicon with sodium hydroxide, in the subsequent generation of hydrogen, depends upon the composition of the material, its fineness, the concentration of the sodium hydroxide and dissolved silicon in solution, and the temperature. The plant, of a small size, low cost and of high productive capacity, consists essentially of three parts: the solution tank, the generator and the washer. The merits of the process and comparative cost figures for materials are given. [A. D. S.]

The generation of hydrogen by the reaction between silicon and a solution of sodium hydroxide is a method which has been extensively used in recent years for filling airships and balloons. It is quite generally called the "silicol" process. The cost of materials makes the method expensive but it has several great advantages, especially for use aboard ship and in portable units for field service. Chief of these advantages are the small size and cost of a plant of large productive capacity, and the simplicity of its operation.

Further discussion of the merits of the process will be deferred until the process itself has been described.

[1] Manuscript received January 28, 1922. Presented by permission of the Director of the Bureau of Standards.

[2] Bureau of Standards, Washington, D C.

The principal reaction involved may be represented by the equation:

$$2NaOH + Si + H_2O = Na_2SiO_3 + 2H_2 \qquad (1)$$

This equation probably represents the reaction taking place at the beginning of a run. However, sodium silicate in solution hydrolyzes, giving sodium hydroxide and hydrated silicic acid as indicated by the equation:

$$Na_2SiO_3 + (x + 1)H_2O = 2NaOH + SiO_2.xH_2O \qquad (2)$$

If we combine equations 1 and 2, we have,

$$Si + (x + 2)H_2O = SiO_2.xH_2O + 2H_2 \qquad (3)$$

While these equations may not represent all the complex reactions occurring in the solution, they probably represent the general course of the reaction, which thus appears to be in effect one between silicon and water, the sodium hydroxide serving as a catalyst. This viewpoint is important, since it shows that the relative amounts of alkali and ferrosilicon to be used in practice should be determined by the speed of reaction and the relative cost of the materials, rather than by computing the proportions corresponding to a definite equation.

The reaction taking place in the generator occurs, of course, at the surface of contact of the ferrosilicon and the solution. If there is sufficient solution present to wet the solid completely, it is apparent that the rate of reaction is dependent only upon the amount of surface of the ferrosilicon, the composition of the two phases, and the temperature. Each of these conditions can be independently varied in the laboratory; the progress of the reaction can be accurately determined at all times by metering the gas evolved. The process is, therefore, one of the few industrial processes which can be completely studied by means of small-scale experiments, and the results extended without appreciable error to operations on a large scale.

A study of the effect of each variable condition has been made at the Bureau of Standards, as a result of which it is possible to predict the course of the reaction under any given conditions with almost mathematical certainty. For a complete account of

these experiments and the application of the results to the problems of generator control, reference should be made to Report No. 40 in the fourth annual report of the National Advisory Committee for Aeronautics. Reprints of this article can be obtained from the Bureau of Standards by those interested.

The plant required for the production of hydrogen consists of three principal parts—(1) the solution tank in which the sodium hydroxide is dissolved, (2) the generator proper in which the reaction takes place, and (3) the washer or condenser in which the evolved gas is washed with water and cooled before being stored or used. The parts are so arranged that liquid can be run into the generator from the solution tank by gravity. The generator is usually provided with an adjustable feed mechanism which places the ferrosilicon feed under the immediate control of the operator. A cold-water spray for diluting the contents of the generator and regulating its temperature is also provided.

The operation of the generator is as follows: A predetermined charge of sodium hydroxide and water is stirred together in the solution tank until solution is complete. A part or all of the solution is then run into the generator and ferrosilicon added at such a rate as will best control the evolution of the gas. The heat of solution of sodium hydroxide is sufficient to start the reaction with ferrosilicon. The heat of this reaction increases the temperature rapidly, a large amount of water is evaporated, and it soon becomes necessary both to cool and dilute the contents of the generator. This is done by means of the water spray mentioned in the preceding paragraph. Care must be taken throughout the reaction that the contents of the generator do not foam over.

It is quite possible, but entirely unnecessary, to carry out the reaction under conditions which will materially decrease the quantity of hydrogen obtainable from a given sample of ferrosilicon. The yield of hydrogen is therefore practically dependent only upon the composition of the solid; but it is by no means proportional to the silicon content. A ferrosilicon containing 90 percent or more of the element yields nearly theoretical quantities of hydrogen; one containing less than 75 percent is almost useless for this purpose.

The rate at which a given weight of ferrosilicon will react depends upon the composition of the material, the fineness to which it is ground, the concentration of both sodium hydroxide and dissolved silicon in the soultion, and the temperature.

In spite of the many conditions affecting the rate of reaction of a given amount of ferrosilicon, the rate of evolution of gas during the major part of the generator run is primarily a function of the rate of feed of ferrosilicon. Whatever the conditions of temperature and concentration of solution, provided they are reasonably constant, and whatever the composition and fineness of the ferrosilicon, if the ferrosilicon feed is regular the material will accumulate in the generator until the amount of reacting surface is such that the rate of solution will closely approximate the rate of addition. Whether the rate of solution is greater or less than the rate of addition of material depends upon whether conditions are changing to make the rate of reaction per unit weight of ferrosilicon more or less rapid. If full advantage is to be taken of generator and condenser capacity it is essential that the rate of generation of hydrogen be as uniform as possible. To accomplish this it is necessary to so choose generating conditions that equilibrium will be quickly reached without generating gas at an excessive rate; that there will be no sudden variations of generator conditions, particularly of temperature, which will greatly disturb the established equilibrium; and that the material in the generator after the ferrosilicon is all added will be quickly and completely exhausted.

Temperature Control During Generation.

The first requirement of successful operation is that the temperature of the generator be quickly raised at the beginning of the run to the point at which equilibrium is to be established, and that this be done without accumulating a large surplus of ferrosilicon in the generator. The ideal procedure is, of course, so to adjust conditions that when the temperature reaches the desired point, the amount of ferrosilicon in the generator will be just sufficient to produce hydrogen at the average rate for the run.

If the generator temperature is to be brought up only by the heat of solution of sodium hydroxide and the heat of reaction

with ferrosilicon, it will be best to start with as concentrated a solution as can be quickly prepared and to use only a part of the solution with a comparatively large amount of ferrosilicon until the temperature reaches that at which it is desired to establish temperature equilibrium. The ferrosilicon feed may then be started and more solution and water added as required to keep the temperature at the desired point.

The temperature chosen for equilibrium should be determined by the following considerations:

(a) It is desirable to have the rate of reaction per unit weight of ferrosilicon as rapid as possible at the end of the run in order to avoid waste of time and material.

(b) The rate of reaction per unit weight of ferrosilicon at the end of the run can be made a maximum for the solution of given concentration by permitting the temperature to rise until thermal equilibrium is established between the heat of reaction on the one hand and the heat of vaporization and other heat losses on the other.

(c) The rate of reaction per gram is increased by increasing the concentration of the solution, but the allowable change in this direction is strictly limited by the fact that concentrated solutions containing much dissolved silicon become very viscous. It is probable that to utilize the materials economically the solution at the end of the reaction should never contain more than 33 parts of sodium hydroxide per 100 parts of water (a 25 percent solution). Twenty-five parts of sodium hydroxide per hundred of water (i. e., a 20 percent solution) would be a safer limit.

(d) The temperature must be kept from changing rapidly at any time after equilibrium is established. This is most readily accomplished by keeping it nearly uniform, and in order to fulfill the other requirements this working temperature must be slightly below the temperature at the end of the run.

The hydrogen leaving the solution is, of course, saturated with water vapor at the vapor pressure of the solution. Most of the heat of reaction is dissipated in producing this evaporation. The temperature at which the heat of evaporation of the water will be equal to the heat of reaction for a solution of given strength at a given barometric pressure can be computed from

the data in any set of physical-chemical tables. For a 25 percent solution of sodium hydroxide at 760 mm. pressure it is about 98° C.

The temperature of the generator should be allowed to rise at the beginning of the run to within 2° or 3° of the maximum temperature possible for the solution of the concentration desired at the end of the run. The temperature should be kept at this point by means of the water spray until the amount of water required is very small. The water should then be turned off entirely and the temperature allowed to rise gradually, as it will do. If this point is reached before the run is half over and the discharged sludge is notably viscous, a lower operating temperature should be chosen for the next run. If water cooling is required until the end of the run a higher operating temperature should be maintained.

A serious mistake was made when the silicol method was first used by employing too high a temperature in the generator. In some cases a temperature of as high as 150°C. was employed and recommended. The practice seems to have been based on the idea that hydrogen could be generated more rapidly at the higher temperatures because an increase of temperature so greatly increases the rate of reaction of a given quantity of solid and solution. The application of this idea to speeding up production as a whole is, of course, correct only in case all the ferrosilicon and all the solution are brought together at the same time. High temperatures in the generator are possible only when the solution is allowed to become very concentrated. Under this condition the sodium silicate is but slightly hydrolyzed and economy of sodium hydroxide is impossible. The solution also becomes very viscous, the particles of solid become coated with the products of reaction and the whole reaction slows down. Unless care is exercised the whole mass will puff up like bread dough, and if it is allowed to cool in that condition it assumes the mechanical characteristics of molasses taffy. It is then so difficult to dissolve that it is usually removed from the generator with a hammer and a chisel.

Starting the Reaction in the Generator.

If time is of great importance, as it often is in military practice, an initial charge of ferrosilicon may be run into the generator

while the sodium hydroxide is being dissolved. The amount of this initial charge should be so proportioned to the sodium hydroxide solution introduced at the start that when the generator temperature reaches the desired equilibrium value the rate of reaction will be the desired average rate for the run. About 15 grams of silicon per liter of solution will be required to bring the temperature up each 10°C.

The initial rate of reaction of any lot of ferrosilicon under generating conditions is easily determined by testing a small sample in the laboratory. In airship practice the little trouble required to determine a proper initial charge for each new lot of material purchased would be well worth while both to save time when time may be very important, and to guard against the danger of a violent reaction which may damage the balloon.

If the usual practice is followed of starting the generator by feeding silicon at an unknown rate, and cutting down on the rate only when the hydrogen production becomes as rapid as desired, the solid may accumulate in dangerous quantity before a temperature of rapid reaction is attained. It is simply a case of a time lag which can be accurately allowed for by computation but not very easily guessed. In one instance an operator is known to have started a continuous feed into a cold generator and to have continued for over half an hour before the reaction became appreciable. Then everything boiled over.

Composition and Fineness of Ferrosilicon.

If the best conditions of temperature control and generator operation indicated above are adhered to, the relative advantage of using ferrosilicon having different rates of reaction because of differences in composition or fineness is easily determined. If the temperature is fairly high, it is only necessary to add, at the start, the amount of material determined in accordance with the principles just discussed.

The temperature will then quickly rise to the desired value, the time wasted with the more slowly reacting material being practically negligible. If the temperature is very low, however, it can not be quickly raised with a slowly reacting material except by introducing so large an amount that the rate of reaction becomes

excessive when the generator once gets hot. In some cases it might be impossible to produce sufficient reaction with low grade material to balance surface heat losses; it would then be impossible to operate the generator at all unless heat were supplied from some external source, or by the reaction between aluminum and sodium hydroxide which takes place at low temperatures. If such a source of heat is available or if weather conditions are not extremely unfavorable, there is little advantage, so far as the initial stages of generation are concerned, in using a high grade or finely powdered material, over the use of an equivalent quantity of a less active solid.

When once the reaction is proceeding at the desired rate, and the temperature and rate of addition of ferrosilicon are kept constant, it is obvious that generation will proceed at the same rate for any material until all the ferrosilicon has been fed into the generator. The amount of ferrosilicon present is then inversely proportional to the rate of reaction per gram of material, and at whatever time the run is stopped the amount of material wasted in the two cases is in this same ratio. The amount wasted at the end of the reaction is not large if a reasonable time is allowed for the reaction to cease. With material such as is generally used by the Army and Navy the loss is certainly not more than one or two percent if ten minutes is allowed to complete the reaction after an hour's run.

Amount of Sodium Hydroxide Required.

The amount of sodium hydroxide required to react with a given weight of silicon has generally been overestimated; perhaps partly because of a tendency to follow the chemical equation for the formation of normal sodium silicate, chiefly because of the early practice already alluded to of allowing temperatures to become so high that little hydrolysis of the sodium silicate was possible. The most economical ratio of sodium hydroxide to silicon will vary somewhat with the price of materials and certain other conditions, but generally speaking not more than an equal weight of the alkali should be used. If a plant were used for practically continuous operation, the ratio of sodium hydroxide to silicon could be still lower.

Construction of Generating Plant.

The generators are usually cylindrical welded tanks of sheet steel having a cubic capacity approximately equal to the maximum volume of hydrogen (measured at normal conditions) to be produced per minute. A mechanical stirrer is always provided to prevent the solid settling to the bottom and possibly caking in the presence of a limited amount of solution. A cold water spray must also be provided in the generator. The tank for dissolving the sodium hydroxide is usually about half the size of the generator proper and should be equipped with a stirring mechanism and with a perforated basket of such size as to have an annular space 3 or 4 inches wide between the basket and the tank wall. The stirring mechanism should be designed to give rapid circulation upward between the walls of the basket and the containing tank.

The gas cooling system should be designed to condense an amount of steam corresponding to the entire heat of reaction amounting to 4.9 kilogram calories per gram molecule of silicon.

The only feature of construction which appears to have given much trouble in the past is the ferrosilicon feed. The ferrosilicon is a pretty good abrasive which rapidly wears out any moving parts with which it comes in contact. In addition it is impossible to keep it dry since a large amount of steam is always condensing in the cooler parts of the generator. If a little alkali also gets into the material a thick dough is formed which it is very difficult to do anything with. Consequently all dry feeds which have been tried have been rather unsuccessful. The most common practice at present is probably that of agitating the ferrosilicon with water and delivering it into the generator as a suspension, the feed being regulated by the opening of the inlet valve. It is almost impossible to maintain a uniform rate of feeding however, and toward the end of a run when it is no longer desirable to introduce water into the generator a very considerable amount is necessarily added.

Much better results may be obtained with the very simple device of a vertical jet of water playing upward into the hopper from which the ferrosilicon is delivered. A horizontal pipe located just above the valve through which the ferrosilicon is fed

has a single hole in its upper surface. A much smaller jet directed downward may be used to keep the valve open. As long as there is solid material directly above the jet the water is playing directly upon the bottom of the powder. When a hole is washed entirely through the solid the jet impinges on the cover of the hopper and is dashed into spray which washes the powder uniformly from the sides into the center. The feed is easily regulated by varying the pressure on the jet and for a given setting of the jet is nearly uniform until the hopper is almost completely emptied.

Merits of the Silicol Process.

The ferrosilicon method is especially adapted for military and naval use because of the relatively small size and low cost of the generator required to produce hydrogen at a rapid rate, the small operating force required, and the fact that no power is used except the small amount required to operate the stirring and pumping machinery. These advantages make it possible to quickly generate sufficient hydrogen to fill a balloon with a generator which can be transported on a motor truck.

The fact that none of the materials used are by themselves combustible, that they do not give off hydrogen until mixed, and that they are easily and safely transported and handled, makes the method especially safe and valuable for use aboard ship. The low cost of the generating plant also makes the method of value for shore stations where the demand for hydrogen is very irregular and the cost of an electrolytic or other plant capable of meeting the maximum demand would be excessive.

The gas is also of exceptional purity, being practically equal to electrolytic gas in this respect. Traces of phosphine and acetylene are about the only impurities likely to be found, although other hydrocarbons may occur to a slight extent and arsine is a possible impurity.

The only considerable disadvantage of the method is its cost. With 85 percent ferrosilicon costing $200 per ton and sodium hydroxide costing $4.00 per hundred pounds, the cost of materials for 1000 cu. ft. of hydrogen at 60° F. and 30 inches pressure will be $4.60 for ferrosilicon and $1.50 for sodium hydroxide, a total

of $6.10. When transportation and handling charges for the materials are added the cost for materials alone is not likely to be less than $7.00 per thousand cubic feet. The labor and capital charges on any plant which is used steadily becomes negligibly small. In any case they will probably be less than for any other method of generating hydrogen.

If the cost of producing ferrosilicon could be reduced, say to $75 per ton of silicon, the process would at once assume industrial importance. In an industrial plant producing large quantities of hydrogen it would be possible and worth while to recover a considerable quantity of sodium hydroxide from the sludge.

The disposal of the sludge is another somewhat difficult problem. The strong alkali is destructive of both animal and vegetable life and cannot with safety be dumped into small streams. Its possible industrial value as a cheap but impure alkali will not justify its transportation to any considerable distance. It could be rendered harmless by neutralization with waste acid materials of any kind or by the addition of calcium chloride.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

A NEW METHOD OF DETERMINING THE RADIUM CONTENT OF CARNOTITE ORES AND OTHER PRODUCTS OF LOW ACTIVITY.[1]

By Victor F. Hess.[2]

Abstract.

When carnotite or other materials are filled into the space between two concentric spheres, the gamma ray effect in the center of the inner sphere can be calculated. This formula was taken as the basis of a direct method of determining the radium content of these substances. The samples were filled in wooden containers which were closed hermetically. The gamma ray electrometer was introduced into the center. The observed ionization, expressed in absolute units (E. S. U.) reduced to normal pressure and temperature, multiplied by certain constants, gives directly the radium content per gram of material.

The method is sensitive enough to give correct figures for material with 10^{-10} g. radium per gram of material. It is very simple, and requires no chemical treatment of the samples before the measurements.

The results on ore samples were compared with the results derived from the chemical analysis of the uranium content, and were found to be in good agreement.

Among the different methods used in radioactivity, the so-called gamma ray method takes the most important place. It exceeds all other methods in accuracy, reliability and simplicity. Relatively few attempts have been made so far to increase the sensi-

[1] Manuscript received March 8, 1922.

[2] Consulting Physicist of the U. S. Bureau of Mines, Chief Physicist of the United States Radium Corporation, Orange, N. J.

tivity of this method, because even the simplest arrangements, consisting of a leaf electroscope and ionization chamber, are sensitive enough to measure the present medical or commercial preparations. In the course of the radium extraction process, products must be measured which have a very small concentration in radium. The author recently has applied the gamma ray method[3] to these cases of low grade radium-barium salts, the content of which varies between 10^{-5} and 10^{-7} grams of radium per gram of salt.

The question now arises, is it possible to determine the radium content of ores like carnotite, or products with even less radium per unit of weight (10^{-10} g. Ra/g.) by means of a gamma ray method? Observations of the so-called penetrating radiation from the earth[4] have shown that even the minute amounts of radium and thorium products in ordinary rocks suffice to give a noticeable effect, due to gamma rays, on very sensitive instruments. Now, since carnotite contains about 1000 times as much radium as granite, the task seems to be an easy one. On the other hand it must be borne in mind that in all measurements of the penetrating radiation from the soil the integral-action of the half-infinite space formed by the soil itself is observed. This gives ionization effects of 2-15 ions per cubic centimeter per second, which correspond to currents of 10^{-15} amperes.

When we consider the fact that gamma rays in solid substances like rocks or ores, are absorbed rather easily, we may conclude that relatively shallow layers of ore will produce more than one-half of the total effect which would be obtained with an infinite thickness of the layer.

Our instrument is surrounded by a large container, filled with ground or coarse ore so that the thickness of the active layer all around the apparatus is sufficient to give a noticeable ionization in the center where the apparatus is placed. It will be advisable to choose a small ionization chamber, otherwise the amount of ore required to surround the vessel on all sides would become

[3] Paper read before the American Physical Society, New York, Feb. 25, 1922.

[4] See McLennan and E. F. Burton, Phys. Rev., 1907, **16**, 184.
A. S. Eve. Phil. Mag. **21**, p. 26. (1911). Th. Wulf, Phys Zeilschr, 1909, **10**, 997.
V. F. Hess, Phys. Zeitschr, **12**, p. 998., **13**, 1084, **14**, 610, (1911-1913).

too large and not easy to handle. Furthermore, it may be stated emphatically that this method is applicable in those cases only where no appreciable amount of thorium is present beside the radium. Thus it can be used for carnotite and also for pitchblende, the most important ores of radium. Both contain practically no thorium products.

THEORETICAL FOUNDATION OF THE METHOD.

To begin with, the action of a spherical shell of radioactive material on a point in the center of this sphere shall be calculated. Fig. 1 gives a cross-section of this arrangement. The shaded space between the two outer circles marks the place where the radioactive material, for instance ground ore, is filled in. The radius of the inner circle, respectively of the inner surface of the two concentric spheres, is called r_o , the outer radius (maximum radius of the container) r_m . In the center of the smaller sphere the gamma ray instrument is placed. The variable r denotes the radial distance of any arbitrary point within the filled container from the center of the apparatus, dr an element of this variable. The coefficient of absorption of the gamma rays within the active layer itself is called μ. This value has to be determined by experiment. The amount of radium per unit of volume of the active material is called ρ, and is expressed in grams of radium per cc. The apparatus which is placed in the center of our arrangement has to be calibrated in terms of radium. A. S. Eve[5] determined the number of pairs of ions produced by the gamma rays of 1 g. of radium (in equilibrium with its successive products) at 1 cm. distance and found this number equal to $K = 4.0 \times 10^9$ pairs of ions per cubic centimeter per sec. This figure was obtained with an ionization chamber the walls of which consisted of very thin aluminum foil, in order to diminish secondary rays. With the usual brass or zinc vessels much higher values are obtained, and for any special type of ionization vessel used in these experiments this constant, which is called "Eve's number," has to be determined by experiments.

Taking an elementary spherical shell of the thickness dr (as

[5] A. S. Eve, Phil. Mag. (6) 1906, **12**, 189; 1911, **22**, 551; 1914, **27**, 349.

marked in Fig. 1 by dotted lines), the amount of radium within this shell is $4.\pi.r^2.\rho.dr$, and its gamma ray action at the center, taking into account the absorption in the layer $r - r_o$ and the distance law, follows:

$$dq = \frac{4\ K.\pi.r^2.\rho.dr \times e^{-\mu\ (r - r_o)}}{r^2}$$

To obtain the total ionization caused by the spherical shell of the thickness $r_m - r_o$ we have to take the integral

$$q = 4\ \pi.\rho.K.e^{\mu r_o} \int_{r_o}^{r_m} e^{-\mu r}.dr$$

or

$$q = \frac{4\ \pi.K.\rho}{\mu} \times \left(1 - e^{-\mu(r_m - r_o)}\right) \qquad (1)$$

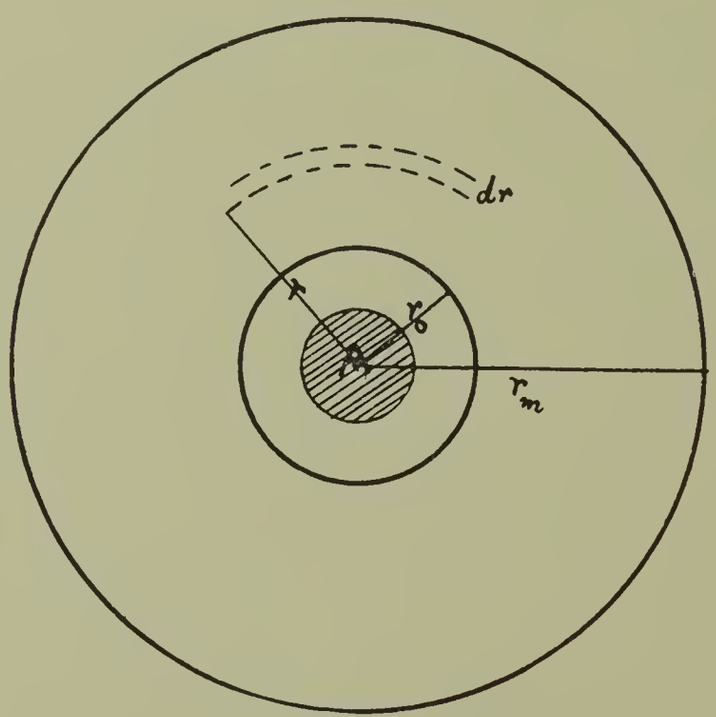


Fig. 1

This ionization is determined experimentally by observing the saturation current i within the ionization vessel, the volume of which is called v. When C denotes the electrostatic capacity of the instrument, and ϵ the elementary electric charge, taking Millikan's value, $\epsilon = 4.774 \times 10^{-10}$ E. S. U., we have

$$i = q.\epsilon.v$$

On the other hand, when we call dE/dt the rate of discharge of the instrument expressed in volts per second, we have also

$$i = \frac{1}{300} \times C \frac{dE}{dt}$$

Thus we find the unknown amount of radium per unit of volume (expressed in g. of radium per cubic centimeter).

$$\rho = \frac{\mu . C.\ dE/dt}{1200\ K\ \pi\ \epsilon\ v\ [1 - e^{-\mu\ (r_m - r_o)}]} \qquad (2)$$

Usually, not the content of radium per cc., but per gram of ore, is desired. If s is the specific gravity of the radioactive material, for instance of the ground ore, and σ the amount of radium, expressed in grams per gram of material, we can replace ρ by $\sigma . s$ and find

$$\sigma = \frac{\mu . C.\ dE/dt}{1200\ K\ \pi\ \epsilon\ v\ s\ (1 - e^{-\mu d})} \qquad (3)$$

In this formula d is taken as an abbreviation for the thickness of the radioactive layer:

$$d = r_m - r_o.$$

This formula gives the radium content per gram of material, when the saturation current in the center of the concentric spherical shells is observed.

APPLICATION TO PRACTICAL USE.

It is important to use an instrument of rather small volume and high and constant sensitivity, which is portable. These conditions are fulfilled only in string electrometers. It was found advantageous to use the gamma ray electrometer devised by the author several years ago, which combines small volume with small electrostatic capacity (1 cm.) and sufficient sensitivity.

Taking an estimated value for the coefficient of absorption in ores ($\mu = 0.06$ cm.$^{-1}$) one can see that a layer of 15 cm. thickness would give at least more than one-half of the effect of an infinite layer. Layers of 15 cm. (6 in.) are therefore sufficient for practical use.

Containers of spherical shape cannot be made up without considerable cost. Furthermore, the construction of a double sphere,

in the center of which the gamma ray instrument can be placed, is also difficult from the technical standpoint. Therefore, experiments were started with a cubical container, consisting of a wooden box made tight by special tar paint. On the front side a kind of wooden inlet was provided, just large enough to slide the instrument in and out. The inlet was 15 cm. (6 in.) wide by 15 cm. deep, and kept tightly closed, so that no radioactive dust could come in contact with the instrument when it was in its position in the center of the box. The lid of the outer box was screwed on and pressed down by steel clamps.

It was found that this procedure served rather well for the purpose of accumulating the emanation within the box. The material is protected against diffusion; nevertheless changes in the temperature and pressure may cause slight losses of emanation. To obtain an estimate, we take the extreme case that the temperature inside the box has changed by 30° C. from one day to the other. The air in the box might contain 10 percent of the total amount of emanation which is in equilibrium with the total amount of radium contained within the ore. When the air inside is heated to 30° C. 10 percent of it escapes; but the amount of emanation in this case would be only 1 percent of the equilibrium amount. Therefore, this temperature influence may be neglected.

When fresh material from the extraction process, like sands or slimes, are filled into the box, losses due to changes in temperature and pressure may sometimes become more serious, because these substances are moist and contain at the time of the first measurement usually less than 50 percent of the equilibrium amount of emanation. But generally it was found, in the course of experiments with more than 150 samples of this sort, that the regeneration of the gamma ray effect as observed by the electrometer follows closely the law of recovery of emanation, as is seen also from Table I.

The thickness of the wooden boards, forming the inlet for the electrometer, was 1 cm. The distance between the walls of the outer and inner box was all around 15.24 cm. When the ore or other material was filled into the space between the outer and the inner box, the thickness of the radioactive layer was also 15.24 cm. all around. Only at the corners the thickness was greater than in the theoretical case of the concentric spheres.

CALIBRATIONS AND CORRECTIONS.

(*a*) *Calibration of the instrument.* The gamma ray electrometer was calibrated by means of radium tubes (2—50 mg.) which had been compared with the National Radium Standard in Washington. By using these tubes at different distances from the center of the gamma ray instrument (0.3 to 2.5 m.) it was first proved that the inverse square of distance law did hold with sufficient accuracy, provided that the apparatus was not placed near the walls of the room where secondary gamma rays always create disturbances. The walls of the instrument consist of zinc, 3 mm. thick. Disturbances from beta rays, therefore, are excluded.

Using the given data for the electrostatic constants of the electrometer actually used (capacity, sensitivity in volts per scale division, volume of the ionization chamber) the value of "Eve's number" for the given instrument at a temprature of 20° C. and a pressure of 760 mm. was found to be $K = 5.55 \times 10^9$ pairs of ions per cu. cm. per sec. for one gram of radium.

This value is naturally higher than Eve's value for a thin-walled aluminum chamber, according to the increase of secondary rays from brass and zinc. Taking our formulas (1) to (3) we have to use this higher value of K.

(*b*) *Absorption Experiments.* In the final formulas (1) to (3) is contained the coefficient of absorption of the gamma rays in the material used. This coefficient, as well as the average specific gravity of the material, has to be determined experimentally.

Experiments were performed in the following way. The material was filled into wooden boxes of different dimensions, and placed between the instrument and the radium preparation (50 mg.), which was kept in constant position 2.5 m. distant from the instrument. Readings were taken without and with the radium in position, and after subtracting the normal leak plus the weak action of the small quantity of ore in the box, these were plotted against the known thickness of material in each case. Fig. 2 gives as an example the absorption curve in ground ore. In this diagram the thickness of the absorbing layer is chosen as abscissa, the logarithm of the respective ionization current i as ordinate. It is seen that for a thickness of 29 cm. of ore the

absorption follows the exponential law very closely. Similar curves were obtained with sands and other materials occurring in the radium extraction.

A comparison of the absorption coefficients obtained with ores, sands, etc., of different specific gravity in a great number of

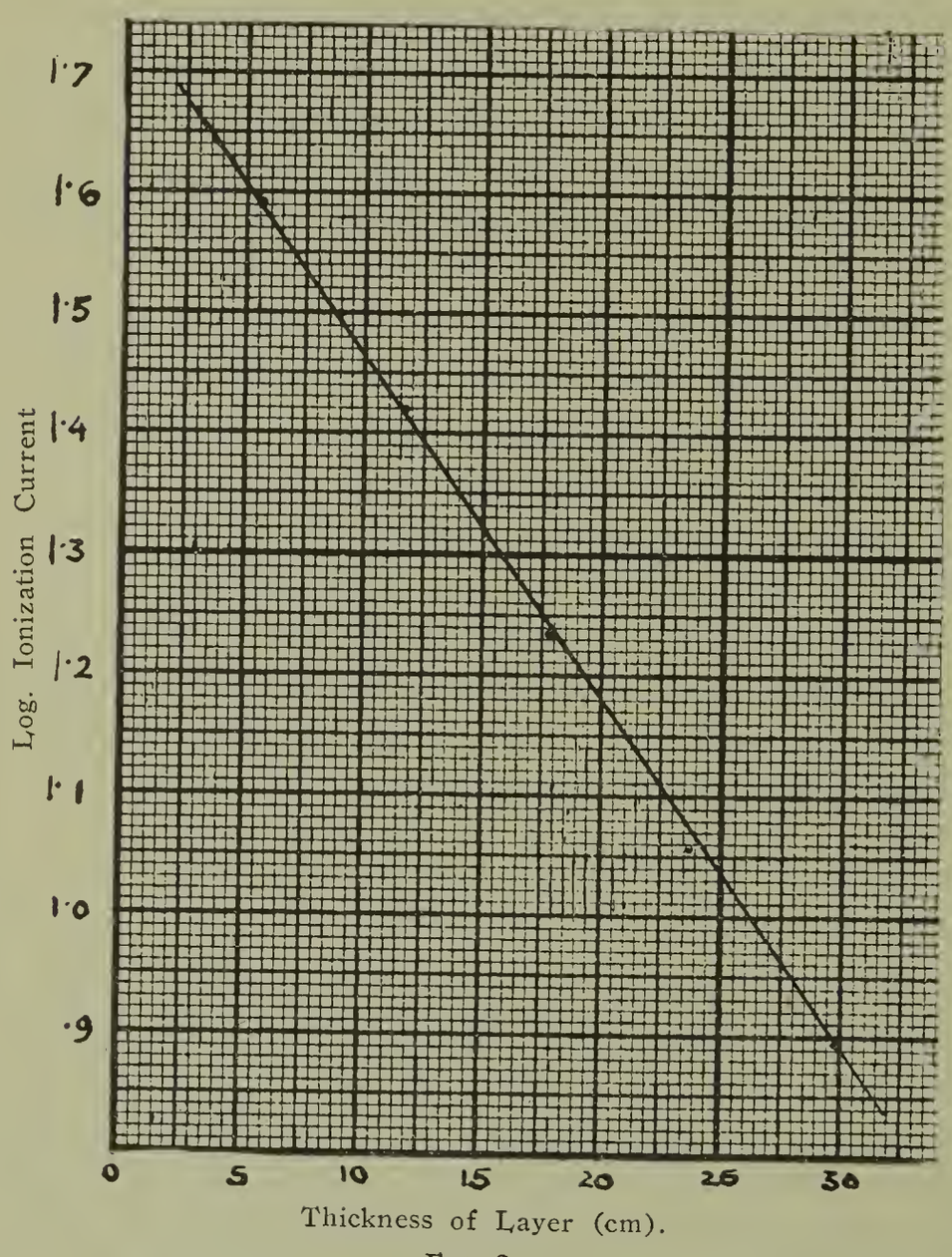


Fig. 2

experiments showed that the ratio $\frac{\text{absorption coefficient}}{\text{specific gravity}}$ was constant within the limits of experimental error. This ratio was found to be

$$\frac{\mu}{s} = 0.045$$

This value agrees very well with figures given by F. Soddy and A. S. Russell, S. J. Allen and others, for substances of similar composition. The constancy of the ratio μ/s is an empirical law, which holds approximately for substances which do not differ too widely in their chemical and physical properties.

Now since the experiments showed that this ratio was constant within the limits of experimental error for all substances used in this investigation, we are allowed to take the given value of μ/s as a general constant, and to derive in each individual case the actual value of μ by multiplication with s, the specific gravity of the sample within the box.

μ and s occur in the general formula (3) in the term

$$\frac{\mu}{s\ (1\ e^{-\mu.d})}$$

Since s varies for ores and sands between about 1.1 and 1.7, it is easy to prepare a table or a diagram which contains the values of this term for materials the density of which is known.

(*c*) *Correction of observed ionization currents for normal pressure and temperature.* It is advisable to place all sample boxes with ores, etc., in the open air, far enough from laboratories where radium extraction work is done. In this way it is easy to avoid contamination of the apparatus during the measurements. In open air the apparatus is exposed to considerable changes in pressure and temperature. The ionizing effect of the gamma rays varies in the same proportion as the pressure and the absolute temperature of the air within the ionization vessel. If the instrument could be kept absolutely airtight for months after the calibration, no corrections would be necessary.

Since the calibration of the instrument was made at 20° C. and 762 mm. (30 inches) pressure, all readings were referred to these standard conditions. If we call dV/dt the current (expressed in volts per sec.) at the temperature t (°C. above or below the freezing point) and the pressure p (expressed in inches of a mercury column) we obtain the corrected value dE/dt at 20° C. and 762 mm. by means of the formula

$$dE/dt = \frac{30\ .\ 273 \pm t)}{p.293}\ .\ dV/dt$$

These reduced values for dE/dt are to be taken when using the formulas (1) to (3).

(*d*) *Correction for incomplete surrounding.* The hollow space (inlet) in which the gamma ray instrument is placed within the container may be considered as a cube. It is obvious that in our arrangement five sides of this cube were surrounded by ore, while the sixth was kept empty in order to slide the instrument quickly in and out again. The actual conditions of the experiments, therefore, did not correspond fully to the theory from which the formulas were derived.

The proper correction was found by experiment. A thin-walled wooden box, of cubical shape, and of the same size as the area of the inlet, was filled with ore and placed beside the gamma ray apparatus at a distance which corresponded to the actual conditions of the experiments with the large containers. The effect (ionization by gamma rays) of this small box was determined carefully. Then the large container was filled with ore of the same lot, and the effect observed. The sum of the ionizations in both experiments would correspond to the ideal case of complete surrounding. Taking the ratio of this sum to the ionization obtained with open inlet, I found as the average the value

$$A = 1.17$$

In other words, in order to get the total current corresponding to complete surrounding, we have to multiply the current dE/dt with the factor

$$A = 1.17$$

THE FINAL FORMULA.

This coefficient has now to be introduced into formula (3); we then obtain the radium content, expressed in grams of radium per gram of material:

$$\sigma = \frac{A \,.\, \mu \,.\, C \,.\, dE/dt}{1200\ K\ \pi\ \epsilon\ s\ v\ (1 - e^{-\mu d})} \qquad (4)$$

In this formula the constants A, C, K and v are valid for all experiments with one individual gamma ray electrometer.

π and ϵ are universal constants. Taking the numerical constants for our instrument ($C = 1.045$ cm., $A = 1.17$, $K = 5.55 \times 10^9$, $v = 968$ cc.), we may summarize these values into one constant

$$S = \frac{A \,.\, C}{1200 \,.\, \pi \,.\, \epsilon \,.\, K.v} = 1.2656 \times 10^{-7}$$

for the instrument used in this investigation.

The other term in formula (4)

$$L = \frac{\mu}{s \,.\, (1 - e^{-\mu d})}$$

varies with the specific gravity and the absorbing power of the material. The following table gives numerical values of this term. μ/s was taken as 0.045.

Specific Gravity s	L
1.1	0.0849
1.2	0.0802
1.3	0.0762
1.4	0.0728
1.5	0.0699
1.6	0.0675
1.7	0.0653

From this table the right value of L in each individual case can be derived graphically. The specific gravity of the sample has of course to be determined first. We may write our final formula in the abbreviated form—

$$\text{Radium content g. Ra/g. material, } \sigma = S.\ L.\ dE/dt \qquad (5)$$

where S and L are constants and dE/dt denotes the ionization current in volts per sec., corrected for the temperature 20° C. and the pressure of 762 mm. This formula gives the actual radium content (according to the actual amount of RaB and RaC present) at the time of measurement.

When the sample is not in radioactive equilibrium, further correction is necessary, according to the regeneration of emanation within the container. That can be done in the usual way. Measurements with the same sample in the box are taken on two different days (at least two or three days apart). Calling the time of the first measurement t_0 and the "actual radium content"

according to formula (5) at this time σ_0, we have at the time of the second reading (t_1) a slightly higher figure σ_1.

The amount at equilibrium σ, as calculated from the increase of emanation present, is then

$$\sigma = \sigma_0 + \frac{\sigma_1 - \sigma_0}{1 - e^{-(t_1 - t_0) \cdot \lambda}} \qquad (6)$$

where λ indicates the period of emanation expressed in the same units of time as t_0 and t_1. With ores, this correction is usually only about 10 percent of the value of the first reading, provided that the ore is not measured immediately after grinding or heating.

Samples which have been treated chemically before the readings, like the so-called sands and other products of the radium extraction process, are usually very far from radioactive equilibrium. In these cases it is advisable to take several readings with intervals of two days, and to compute the equilibrium for each pair of readings separately by formula (6). The average is then far more reliable. An example will illustrate this fact. Wet material from the extraction was read on five days and the results shown in Table I were obtained.

TABLE I.

Readings on Wet Material.

Date and hour of reading		Radium Content g. Ra/ g.	
		Observed actually	Calculated equilibrium
22.	4.30 P. M.	1.278×10^{-9}	
24.	11.50 A. M.	1.469×10^{-9}	1.96×10^{-9}
27.	Noon	1.710×10^{-9}	2.06×10^{-9}
31.	4.50 P. M.	1.895×10^{-9}	2.06×10^{-9}
4	3.00 P. M.	1.970×10^{-9}	2.12×10^{-9}
		Average.....	.....2.05×10^{-9} g Ra/ per g.

The agreement is a fairly good one, although the actual gamma ray effect at the time of the first reading was only 60 percent of the end value.

THE EXPERIMENTS.

The measurements were carried out in the following way. After taking the normal discharge of the gamma ray instrument, the instrument was charged again and the voltage noted. Immediately afterwards the instrument was placed in the center of one of the filled sample boxes, and exposed there for from 2 to 20 minutes, according to the actual effect observed in a preliminary reading. After exposure the instrument was taken out and read again. The discharge during the time of exposure was always large enough so that the possible errors of reading (0.2 scale divisions) were small compared with the total drop in voltage. Time, temperature and pressure were noted, and the final radium content calculated by means of our formulas (5) and (6).

Very low grade ore (3×10^{-9} g. Ra/g.) gave an actual effect of about 0.3 volt/sec., while the normal leak of the instrument is usually 0.005 volt.

Working at places where the normal discharge of the instrument is not increased by radiations from the surroundings, it is possible to measure radium contents of materials with only 3×10^{-11} g. Ra/g. with an accuracy of 10 percent. This is the lowest grade of radium content for which this method can be used. Actually, this method gave good results with all materials of 10^{-10} g. Ra/g. and more. For materials which contain as much of 10^{-8} g. Ra/g. or more it will be better to use the method described in another paper.[6]

ADVANTAGES OF THE METHOD.

Measurements with the new gamma ray instrument are simple, require very little time (single readings about 10 min.) and may be carried out by anybody after a short training. The material can be tested directly, without decomposing or other chemical treatment. Additional errors which arise in using the emanation method, such as the necessity of diluting several times, possibility of precipitation of radium during the time of accumulation in the solution, etc., are totally avoided. Compared with Joly's "melting method," our method requires very little experimental equipment.

Our method gives the average radium content of rather large

[6] Phys. Review (2) Vol. 19 (1922).

samples, 91-136 kg. (200-300 lb.), when layers of 15 cm. (6 inches) are used. When the average radium content of a whole carload of ore is desired, it is easy to prepare a good average sample in this case, while preparation of small samples for chemical analysis or for the emanation method requires great care.[7]

TABLE II.

Comparison with Uranium Analysis.

Sample No.	Radium Content in Mg. Per 1000 Kg.	
	Gamma Ray Method	Uranium Analysis Method
1	3.49	3.61
2	3.50 3.44 3.48	3.35
3	4.00	4.28
4	4.47	4.49
5	6.22	6.14
6	4.91	4.93
7	5.92	6.02
8	7.00	7.68
9	5.93	6.80
10	9.40	10.1
11	7.06	7.17

CONSIDERATION OF POSSIBLE CAUSES OF ERROR.

The method can primarily be used only for materials which do not contain thorium products in addition to radium. The thorium content of the minerals chiefly used in the extraction of radium (carnotite and pitchblende) is entirely negligible.

The gamma ray instrument was calibrated by radium tubes which contain all successive products, RaA-RaC. Now, when testing an ore we may have one other substance which gives off gamma rays: Uranium X_2. Its rays are not as penetrating as the gamma rays of RaC. And the intensity of ionization given by these rays is comparatively much less than that for the equilibrium amount of RaC. Direct determinations of the total ionization of the gamma rays of UX_2 as compared with the equivalent amount of Ra or RaC respectively, have not been made so far. But the efficiency of gamma rays, compared with that of the beta rays, has been tested for RaC and UX_2 separately, and Soddy

[7] U. S. Bureau of Mines, Bulletins Nos. 103, 104 (1916-17).

and Russell found[8] that taking the ratio for RaC as unity, then for UX_2 it would be 0.02, or, much less intense are the gamma rays of UX_2 as compared with the gamma rays of RaC. Thus we may conclude that the gamma rays of UX_2 play an inferior and negligible role in our experiments with ores.

COMPARISON WITH CHEMICAL METHODS.

Table II gives a number of chemical method results compared with the results of our gamma ray analysis.

From Table II it is seen that the results of the two methods agree on the average within 5 percent. In 8 cases out of 11 the agreement is even better.

In general, with the gamma ray method a slight tendency to give lower values than the calculation based upon the uranium analysis may be noticed. Further experiments with both methods will be carried out. At present it cannot be decided whether the lack of agreement in the samples 8, 9 and 10 was due to inaccuracy in the preparation of the sample for the uranium analysis or to other disturbances (escape of emanation caused by sudden temperature changes in February).

Considering the fact that the quantitative determination of uranium in ores by chemical methods is rather delicate, and subjected to additional errors in sampling, we may conclude that the agreement is as good as may be expected.

The author wishes to express his sincere thanks to his colleague, Dr. Edwin D. Leman, for valuable suggestions in the course of this investigation, and to Miss Elizabeth E. Damon for efficient assistance in the experiments.

Research Laboratory,
U. S. Radium Corporation,
Orange, N. J.

DISCUSSION.

S. C. LIND[1]: The matter of radium determination, as Dr. Hess has stated, is a very important one for all companies engaged in the production of radium. The analysis of radium ores in the

[8] A. Russell and F. Soddy, Phil. Mag. (6) 1911, 21, 130.

[1] Physical Chemist, U. S. Bureau of Mines, Reno, Nev.

various plant products has been a little different from ordinary chemical determinations. You are dealing, in the first place, with concentrations over a tremendous range. In an ordinary plant, you are handling materials of different character, varying in concentration by as much as a billion-fold. In the past we have had two methods in general use. In the first place, the alpha ray method, which is a method just as simple and just as easy to carry out as the one that Dr. Hess has described to you this morning, but it is a method of rather limited application on account of its lack of accuracy. In the second place, we have had the emanation method that Dr. Hess has mentioned, but that is a method requiring an expert to carry out, on account of the difficulty of the manipulation involved. An ordinary chemist without special training is not competent to make these measurements. There are only one or two places in the United States now where they can be done accurately for the general public, though, of course all the companies engaged in the work have made these measurements.

Dr. Hess has really rendered us a great service in proposing this method and working out so beautifully the mathematics of it and indicating the size of the vessels which must be used. Dr. Hess brings out in his paper that for ordinary commercial ores the quantities necessary for this method are very much larger than we ordinarily use, in some cases as much as 200 or 300 pounds for a determination. As Dr. Hess points out in the paper, this has an advantage in that it gives you a better sample of a carload lot of ore and does not necessitate such careful grinding and sampling as is ordinarily used. It has one disadvantage in that these very penetrating gamma rays penetrate the surrounding atmosphere. Each determination must be separated from another by a considerable distance, so that if you have in a plant 50 or 100 determinations going on at one time, you will have to cover quite an area with these various preparations, but that is a difficulty that is not so serious. It also involves a little labor in moving them around, and of late years labor has cost almost as much as the employment of technical men.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

ELECTROMAGNETIC MOTIONS IN ELECTRIC FURNACES.[1]

By Carl Hering.[2]

Abstract.

The subject is supplementary to that of a paper read a year ago. It is described how a new proposed law given in the former paper may be applied to the production, by the current, of certain desired motions such as those for circulating or stirring liquid conductors in a furnace. Guides are given to aid one in determining whether such motions can probably be produced by the current. It is maintained that the former restrictions to only one such motion-producing force, were not justified, and that many others formerly not accepted are possible.

In a paper on Electrodynamic Forces in Electric Furnaces, read before this society at its April, 1921, meeting, the writer described some of the more recently discovered forces of electromagnetic origin which may be detrimental or may be made good use of in those types of electric furnaces in which the current passes through the molten material, and in conclusion briefly mentioned a proposed new law to aid one in dealing with these forces, promising a fuller discussion of the law elsewhere, as this subject pertains to physics and not to electrochemistry. The explanation and discussion of this law with descriptions of various crucial experiments has since been published in the Journal of the Franklin Institute for November, 1921, page 599, under the title of Revision of Some of the Electromagnetic Laws.

The purpose of the present paper is not to discuss this law, as this has been done elsewhere, but to show how it may be

[1] Manuscript received January 16, 1922.

[2] Consulting Electrical Engineer, Philadelphia, Pa.

applied in practice to the production of possible forces for performing desired useful operations, like circulating, stirring, transferring, etc., in electric furnaces. According to the former art only one such force was recognized by physicists, namely a force exactly perpendicular to the axis of the conductor, which could, therefore, move the conductor only parallel to itself and never in any other direction; when the writer showed, some years ago, by experiments, that motions in other directions could also be produced, others either endeavored to explain it as a secondary reaction, or, when that was not successful, they adopted the philosophy of the ostrich, and ignored the experimental evidence.

According to the new law this very narrow restriction to only one force, due apparently to Maxwell, was entirely unnecessary and, therefore, had for the past 50 years closed the door to us to possible developments in new directions, as those who questioned it were at once placed in the same class with proponents of perpetual motions. Hence this new law, if correct, opens up the door to possible new developments which those who valued their reputation would formerly not have dared even to suggest. It should be added here, however, that this new law has not yet received general endorsement, and as it is a heresy to those who have such scriptural faith in all that Maxwell said about 50 years ago, it will no doubt be strenuously opposed by his orthodox disciples. But on the other hand, although it has now been open for discussion for a year, and has been called to the personal attention of many, not a single attack on it has yet come to the notice of the writer. It seems safe to say that if it were incorrect, it would surely have been pointed out by this time by some one of the many staunch orthodox followers of Maxwell.

This law, moreover, is nothing more than a restatement in electrical terms of the old, well-known and generally accepted law of nature that such motions will tend to take place as will reduce the potential energy of the system; in an electromagnetic system the potential energy resides in the flux; the only question seems to be whether the writer's electrical version of it is its correct interpretation or not. The new law is that in a system of electric current-carrying conductors any, and only such, mechanical motions of its conduc-

tors will tend to take place as will generate a counter e. m. f. somewhere in the electrical circuits. But whether or not this electrical version is the best one, the general law of nature on which it is based ought to apply to all electromagnetic systems as well, and it seems to follow in any case that our older restriction to only one possible force, was unjustifiable.

The door being now opened to us to use and develop these formerly outlawed forces, the application of this new law may be of interest to those who may wish to produce electrically some particular motion for a useful purpose, as for instance for the moving, circulating, pumping, or stirring of liquid masses in electric furnaces. Possibly, also, in aqueous electrolytes, though in general these forces, which as a rule increase with the square of the current, become formidable only when the currents are rather large. As for formulas for calculating in advance the quantitative value of these forces, little as yet is known; the formula for calculating the pressures produced by the pinch effect was developed by Dr. E. F. Northrup,[3] but it is limited to only circular cross sections; it is presumably greater for oblong sections. In other cases some approximate idea might roughly be obtained by estimating the mechanical power required to be done by such forces, the electrical equivalent of which in watts then is the product of the amperes (in phase) and the counter e. m. f.; dividing this by the amperes in the circuit gives the counter e. m. f. required, and of course the direct e. m. f. must be great enough to supply this in addition to that required to overcome the resistance and doing any other work. In a certain furnace in which large quantities of molten brass at rest were continuously being put into rapid motion by such a force, it was found that the mechanical power produced by this force was nearly 50 kw., which was nearly half the power input. In a furnace this is not lost, as it is all converted into heat ultimately. It is generally the power and not the force that one desires to know in advance.

To one who is not an electrical engineer and who desires to use some of these forces, the crucial clause in this law referring

[3] Reproduced on p. 257 in the writer's paper on The Working Limit of Electrical Furnaces; these Transactions, Vol. 15, 1909.

to the generation of a counter e. m. f., may not be sufficiently clear to depend upon in practice. In such cases the following general guides and facts may perhaps sometimes be of assistance.

All such mechanical forces are due directly to the magnetic flux encircling every current-carrying conductor or issuing from the poles of a magnet; when these forces act to produce motion (kinetic energy) an equivalent amount of this flux energy or strain must disappear as such; when the flux produced by a current is thus reduced, the current immediately replaces it, and this generates a counter e. m. f. in the circuit. Theoretically the product of this counter e. m. f. and the current (in phase) must be equal to the mechanical power produced. This of course assumes that there are no other counter e. m. f's., such as those due to chemical reactions. The forces of the flux act to move the material of the conductor, hence when this is a mobile liquid, or the vapor of an arc, these forces become more evident.

The so-called lines of force by which flux is usually represented, each line standing for a unit of flux, always make complete circuits which can never be opened like an electrical circuit. These lines tend to contract or shorten like stretched rubber bands; like lines repel each other, and unlike attract; these forces are those which determine the distribution and, therefore, the relative local densities of the flux; they give rise to the mechanical forces, hence, if they are allowed to thus expend their energy, the flux disappears as such, being converted into the mechanical motions produced thereby. Such self-produced motions are always accompanied by a counter e. m. f. The reverse motions could never be produced by the current.

An e. m. f. is always generated when a conductor moves across a flux or a flux moves across a conductor; whether it is a direct or a counter e. m. f. can readily be determined by well known rules; if it is a counter e. m. f. it is likely that this motion could be produced by the current if the necessary freedom of motion can be provided. It is not necessary that this counter e. m. f. must be produced in the moving part, as the motion of one part of a circuit may be produced by the circuit if thereby a counter e. m. f. is generated in some other part.

A counter e. m. f. is always generated when a liquid conductor is crushed by the pinch effect, or when it is lengthened by the

stretch effect, as in both cases some new flux is generated, which is always necessarily accompanied by a counter e. m. f. As an illustration of the force which tends to lengthen a conductor, a vertical U-shaped conductor whose ends dip into two mercury cups, can be ejected almost violently in this way. Theoretically every ampere flowing through a conductor of negligible section and removed from all outside influences, generates a certain definite amount of flux per inch or foot of its path; hence any increase in length increases the flux in the proportion of the increase in length. When the conductor has an appreciable diameter there is some flux in its interior, but the proportion of this increase still holds good.

When two neighboring conductors carrying like currents are allowed to move toward each other, or away from each other, if the currents are unlike, a counter e. m. f. will be produced. A high flux density near a low one should tend to move the conductors so as to equalize the two densities; when thus equalized there is room for more flux which the circuit at once generates, thereby generating a counter e. m. f.; a circuit turning a corner is an illustration (called the corner effect); the flux density in the inside of the angle is far greater than on the outside; such a circuit should, therefore, tend to straighten itself. A small conductor connected to a very large one, like a bath of metal, should tend to move away from the large one, if thereby some new flux around the lengthened part is generated; there is a somewhat abrupt change of flux density at the point of connection.

The tendency of a circuit to lengthen itself as a long compressed helical spring does, may, if the proper conditions of freedom exist, bulge out into a C-shaped path, as such a spring would do; this is sometimes seen in an electric arc. It is even conceivable that it might in trying to lengthen itself form a path like the letter S, as such a spring would do if the freedom of motion was in those directions; in fact, it has been reported that the rails of a street railway assumed approximately this shape when there was a short circuit which caused a momentary immense current to flow.

The skin effect, which confines an alternating current more to the outside surface of a large conductor, may perhaps some-

times add its influence to the motive effect of the flux by changing the current path. The variously defined Hall effect, according to which the location of the path of a current may be changed in its conductor by neighboring magnetic flux, might perhaps also become formidable enough to add its influence under high current density conditions. It is possible that the Hall effect which moves the current path, acts so only when the conductor itself cannot move, and that the same tendency would move the conductor if the necessary freedom of motion existed, as it may in mobile liquid conductors or vapors of an arc.

The position of the solid electrodes entering a molten bath may tend to produce motions in the bath; if the current there turns a corner, the corner effect may become formidable; there is also an abrupt change of flux density at such points. Neighboring magnets or magnetic bodies may have very decided effects on such motions; thus a bar of iron held beneath an open channel of molten material will very greatly increase the pinch effect; or when held above it a small hill of molten metal will rise under it, being maintained apparently dynamically by a continuous upward flow under the bar. This force both lifts and stirs.

The counter e. m. f. is of course produced only when and while there is actual motion (kinetic energy) and not by a mere force (potential energy); hence, before the motion is in full action, which may take an appreciable time when large heavy masses of metal are to be put into rapid motion, there will be little or no counter e. m. f., and, therefore, an abnormally large momentary current, as is illustrated in the starting of a motor. The necessary freedom of motion must of course be provided for in any particular case of a desired motion. Care must of course be taken that a desired motion is not annulled by an equal and opposite effect somewhere else; thus a circuit will not lengthen itself at one place if thereby it shortens itself somewhere else by an equal amount. In this connection, however, it should be added that there are still numerous unknown factors in this new field. For instance, in the case of two neighboring baths of molten material separated by a thick wall, through the bottom of which there was an apparently straight hole connecting the two, the pinch effect caused the metal to rise quite high in one bath,

that is, the flow was in one direction. This may have been due to some accidental dissymmetry or to an accidental existing hydrostatic flow before the start, which the pinch effect then kept up and augmented, as it should. In another case in which the dissymmetry was intentional, this unidirectional flow was invariably in the same direction. Such conditions might be used as a valveless pump for molten materials.

The force of the pinch effect has the peculiar property of tending to move the better conductor to the central axis; thus a copper wire floated on a mercury channel will be sucked down toward the center quite violently when a sufficiently large current passes. This seems to act to separate the good conductors like the metals from the bad ones like the slags; the action is analogous to that in centrifugal separators. Possibly mixtures of metals of different conductivities might be separated in this way.

An electrodynamic force which temporarily virtually increases or decreases the specific gravity of a liquid conductor, can be obtained by creating a strong magnetic field horizontally across a horizontal channel containing the current-carrying liquid conductor. The conductor will in such cases tend to move either down or up, depending upon the polarity of the flux and the direction of the current. If it tends to move down, the effect will be like increasing the specific gravity, causing lighter particles to rise; the particles, like slags, for instance, that carry less current, will become relatively lighter. If this force tends to move the conductor upward, its effect will be like decreasing the specific gravity. The writer does not know of any application of this force in practice at the present time, nor can he give any figures, but it is believed that the increase could be made many fold, and not merely in percentages. It is believed that the specific gravity of acidulated water has been increased in this way about four fold. The relatively different effect on different materials depends, of course, on their relative conductivities. A higher resistivity material, and especially any material not forming a continuous conductor, as for instance the disconnected fragments or globules of materials suspended in the main conductor and having a higher resistivity, like the non-metallic

impurities in steel, would be least affected by such forces and, therefore, rise. Metallic aluminum and its chief impurity, its oxide, which have so nearly the same specific gravity, might perhaps be separated by means of this kind of a force; it is believed, however, that the forces in the pinch effect are quite as effective and are far simpler to produce. It has also been suggested, but apparently was never carried out in practice, to circulate a liquid metal conductor in an electric furnace, by using that force.

The above briefly-stated guides and facts may be of assistance to those who may desire to avail themselves of some of these forces. In general, according to the above law, any desired motion of the conductors (especially of the mobile liquid conductors or arc vapors in electric furnaces) can probably be produced electromagnetically by the current itself, if such a motion would produce a counter e. m. f. somewhere in the circuit, if the necessary freedom of motion exists, and if there is not also produced thereby somewhere else in the system an equal and opposite effect. The original source of energy must of course be able to provide the additional voltage to overcome this counter e. m. f., that is, it must provide the energy for such motions. While theoretically there may be no limit to the intensity of the forces thus produced, in practice there is. A few pounds pressure per square inch will, however, produce quite rapid motions of even heavy molten liquids. Strong forces require large currents, which tend to generate heat; such forces are, therefore, limited largely to furnaces in which this heat is useful.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

THE MEASUREMENT OF PRESSURES IN VACUUM TYPE ELECTRIC LAMPS.[1]

By Duncan MacRae.[2]

Abstract.

The tip of the lamp is removed in an evacuated glass system by means of an iron plunger electromagnetically operated. The resulting pressure is measured with a McLeod gauge and the pressure in the lamp before opening is calculated. The results of measurements on unflashed, flashed, and life tested lamps are given.

In engineering work connected with the development and manufacture of incandescent filament lamps, it is frequently desirable to determine the pressure in an evacuated lamp. A rough approximation is easily obtained by the well-known use of the induction coil; but, heretofore, exact methods of pressure measurement, requiring no modification of the regular lamp construction or interference with production, have been lacking. The method about to be described has been found useful in maintaining a high standard of efficiency in factory exhaust and in interpreting life test results on experimental lamps. It is so simple in practice and principle that it is remarkable that there is no record of its previous use.

The glass system used is constructed of Corning G-702 P and is shown in Fig. 1. An actual measurement is carried out as follows: With the aid of small wedges of glass (not shown) the lamp is adjusted firmly in the lamp holder. Then the ground glass surfaces at *a* are cleaned, greased with a good stopcock

[1] Manuscript received November 28, 1921.

[2] Research Physical Chemist, Research Laboratory, Westinghouse Lamp Co., Bloomfield, N. J.

grease, and carefully fitted together so that the tip of the lamp is in position to be broken off by operating the iron plunger b[3]. The solenoid and plunger are placed in the positions shown in the drawing. The stopcock leading to the mercury vapor jet pump is opened, and after about five minutes the McLeod gauge will show a pressure less than 0.1 bar. Now, after closing this stopcock, about four pressure measurements are made with the McLeod gauge at three-minute intervals, and plotted on a piece of co-ordinate paper. If the points fall on a straight line and

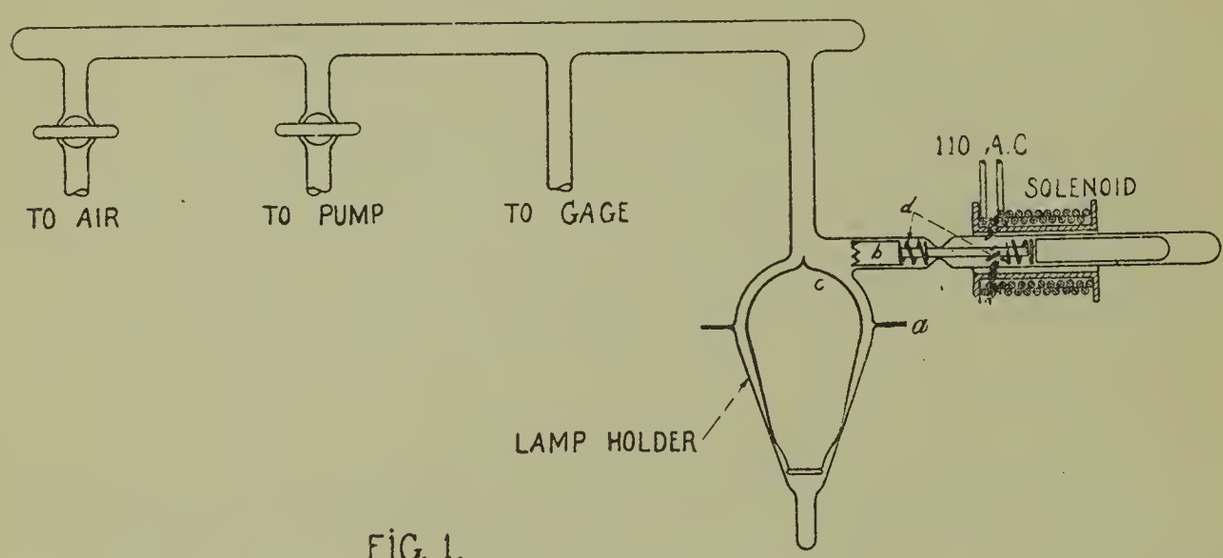


FIG. 1.

show only a slow increase in pressure, all is now ready to break off the tip of the lamp by closing the circuit through the solenoid. The two springs marked d are very necessary to prevent the plunger from breaking the tube holding it. The length of the plunger is so adjusted that it will not strike the glass wall of the system during the operation of removing the lamp tip. One minute after the lamp is opened, another series of pressure readings taken at three-minute intervals is begun and plotted. The pressures p_1 and p_2 are read from the two pressure lines extrapolated to the instant of breaking off the tip.

If V_L is the volume of the lamp and V_S the volume of the system exclusive of the lamp, the pressure in the lamp is given by the equation

$$P = p_2 + (p_2 - p_1) \frac{V_S}{V_L}$$

[3] Compare Z. Physikal Chem. 1907, 60, 23.

The ratio $\frac{V_S}{V_L}$ is determined by opening a lamp containing a known pressure of dry gas, or by determining separately the two volumes.

The composition, quantity, and sources of gases in vacuum type lamps, as well as the removal of such gases, have been discussed by others[4]; but the following examples are of interest as examples of direct measurements by the method just described.

Immediately after exhaust and before the manufacturing operation known as "flashing," pressures corresponding to McLeod gauge readings of 4 to 10 bars are found in well exhausted factory product lamps. These values do not include water vapor or other vapors whose pressure is not indicated by the McLeod gauge, but are useful in comparing different methods of exhaust. Lamps in which pressures of 50 bars or more exist are easily eliminated by the customary test with the induction coil.

The primary object of the "flashing" operation is to insure the proper functioning of the lamp when first lighted on a commercial circuit. It consists of a first lighting of the lamp, during which the chemical substances, such as phosphorus, introduced into the lamp for the purpose of removing residual gases and maintaining the efficiency of the lamp, are activated.

Pressure measurements after "flashing" indicate pressures less than one bar. Indeed, unless, by long evacuation of the system before breaking the lamp, a very low value for p_1 is obtained, negative values will result on applying the equation

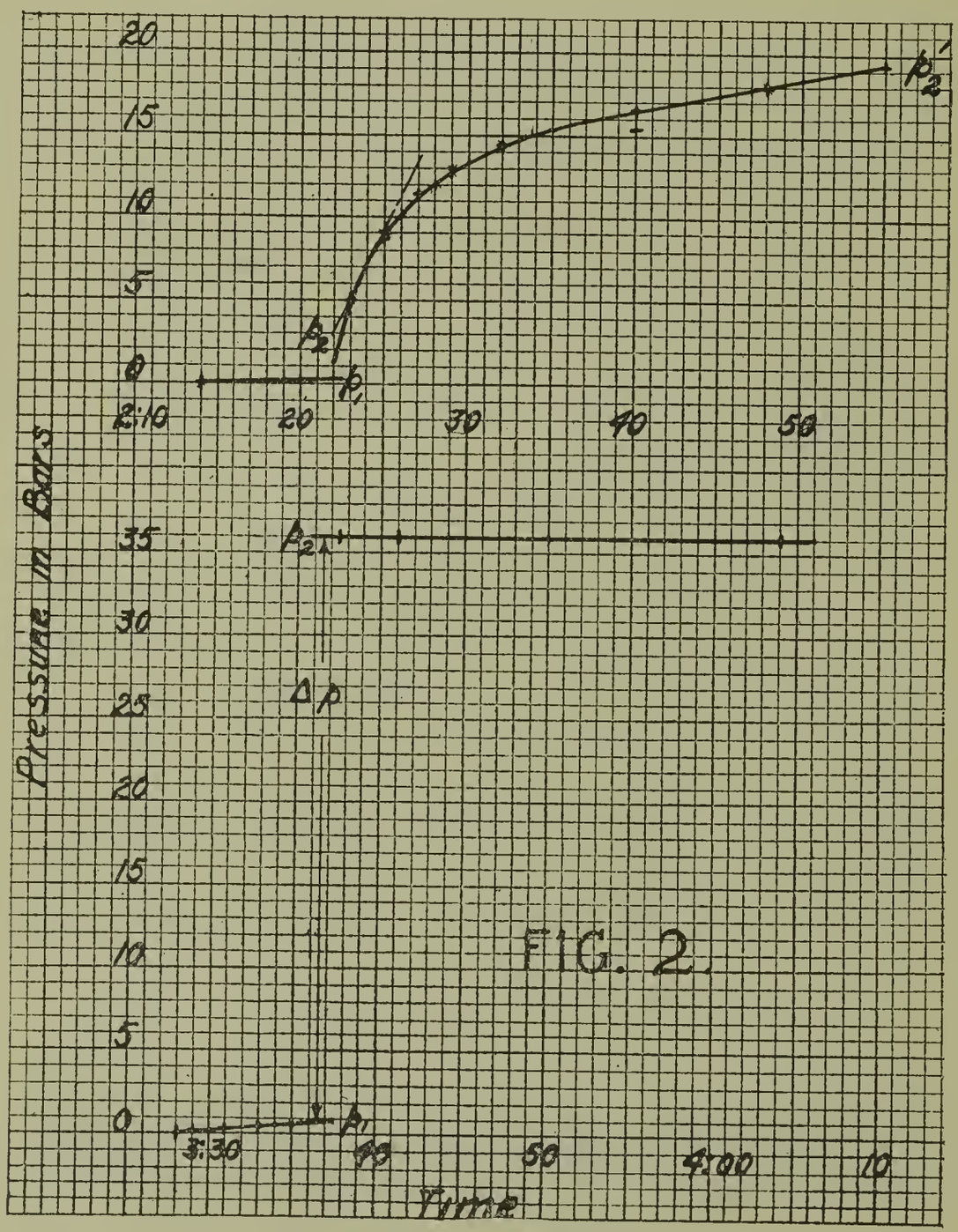
$$P = p_2 + (p_2 - p_1) \frac{V_S}{V_L}.$$

These negative values are the consequence of the reaction of gases (particularly oxygen) with the excess of phosphorus or other "cleanup agent" still in the lamp when its tip is removed.

Pressure measurements on life tested lamps which have burned over 1,000 hours and have shown good efficiency maintenance, give a result of the type shown in the upper diagram of Fig. 2. This indicates a low pressure in the lamp before removing its

[4] W. R. Whitney, Trans. A. I. E. E., 1912, **31**, 921-30; I. Langmuir and J. A. Orange, A. I. E. E., 1913, **32**, 1893-1926; L. Hamburger, Proc. Amsterdam Acad. of Sci., 1918, **21**, 1062-77; N. R. Campbell, Phil. Mag., 1920, **40**, 585-611; 1921, **41**, 685-706.

tip. The gradual rise in pressure after removing the tip has not yet been satisfactorily explained, but is probably connected with some action of the vapors, present in the system (but not shown by the McLeod gauge) which by reaction with finely divided tungsten, or in some other way, give rise to gases such



as hydrogen, whose pressure is capable of measurement with the McLeod gauge. Occasionally, with life tested lamps, a result such as is shown in the lower diagram of Fig. 2 is obtained and its occurrence in the case of a life tested lamp is usually associated with a slightly reduced average efficiency.

I am indebted to Mr. Christopher Kirwer, of the Research

Laboratory of the Westinghouse Electric and Manufacturing Company for the construction of the apparatus, and to Dr. E. L. Harrington, of our Physical Department, for making some of the pressure measurements on unflashed lamps.

DISCUSSION.

C. J. THATCHER[1]: Dr. MacRae, I understand you to say that negative lamp pressures can be explained by absorption of residual oxygen by the phosphorus in the lamp. Such a reaction between residual gases and phosphorus occurs only, however, during flashing; *i. e.,* intensive incandescence of the filament. A great many years ago Van't Hoff made measurements of the vapor pressures obtained when you expose both red and, I believe, also white phosphorus to oxygen. At very low pressures, he found there was no absorption whatsoever. Phosphorus even in the form of vapor does not combine with oxygen at very low pressures except in an ionized atmosphere, which you get by flashing. I think you will have to find some other explanation for the negative pressures, because phosphorus will not take up oxygen. I was the expert in the original patent suits on the Malignani patent, in which that flashing or ionizing operation was first disclosed; and I tried oxygen with phosphorus and its vapor at low pressures, and found that no appreciable combination occurs at the pressures you have in incandescent lamps, except when you ionize; even then the effect is physical rather than chemical. So I do not believe that a chemical combination can be used to explain the negative pressures you observed.

DUNCAN MACRAE: That is the most reasonable explanation that I can think of. Of one thing I am certain, we have no negative pressures in our lamps.

C. C. PATERSON[2] (*Communicated*): Dr. MacRae in writing his first paragraph must have been unaware of the work of Pirani on the hot wire pressure gauge, which was developed, we believe, for exactly the purpose which he described. He must also have been ignorant of the development of the Pirani method which we have described in Proceedings of the Physical Society **33**, 287.

[1] New York City.
[2] Director, Research Laboratories, General Electric Co., Ltd., London.

August 15, 1921. These methods appear to us simpler and quite as accurate as that which he describes and to have the advantage that they measure the pressure of vapors as well as of permanent gases.

Our experience is not in accordance with Dr. MacRae's view (p. 313) that the determination of the permanent gas is "useful in comparing different methods of exhaust." In our experiments the vapors, especially water vapor, have been greater in quantity than the permanent gases and far more variable; a reduction in permanent gas is by no means always accompanied by a reduction in total pressure. In fact when some of the important factors are varied (especially the baking) a reduction in total pressure is accompanied by a slight increase in permanent gas.

We may offer very tentatively an explanation of the upper curve in Fig. 2. In a lamp which has been exhausted with phosphorus the leading-in wires are always coated with phosphide. When water vapor enters such a lamp, PH_3 is generated. If Dr. MacRae's apparatus was not thoroughly dry before the tip of the lamp was broken, we should expect to find a generation of gas when it is broken.

A. L. Feild[3]: In regard to the negative pressure of which Dr. MacRae speaks, I might say that the same effect would be obtained if the pressure in the evacuated chamber were higher than that in the lamp before the latter was broken.

Duncan MacRae: The point that Mr. Feild makes has been taken into account in the equation for calculating the pressure in the lamp.

I would like to reply to three points made in the written discussion by Dr. Paterson. First: the McLeod gauge in this apparatus can be replaced by a Pirani gauge or it can be replaced by a system adapted to the analysis of very small quantities of gas. It is a matter of preference which gauge is used. Second: Dr. Paterson's point in regard to the effect of the presence of water vapor is well taken; and results in its presence should be interpreted with care. Third: the tentative explanation of the slow rise in pressure, as probably due to the interaction of water vapor and a phosphide, is interesting; but does not hold when the phenomenon is observed in a lamp containing no phosphorus.

[3] Carbide and Carbon Res. Lab., Inc., Long Island City, N. Y.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

IDIOMORPHIC AND HYP-IDIOMORPHIC STRUCTURES IN ELECTRO-DEPOSITED METAL [1]

By W. E. Hughes, B. A. [2]

Introduction.

The study of the structure of electro-deposited metal appears to justify, more and more, these three conclusions: (1) The connection between the macroscopic aspect and the internal structure of a deposit is so definite that, by following the changes in the one with the eye, it is possible to know what the changes of the other are. (2) The structure of a deposit in any given case is determined by the conditions of deposition that obtained during its formation. (3) A particular type of structure is not confined to any one metal; it may appear in different metals, and appear as the result of the prevalence of similar conditions of deposition.

The objects of the present paper are to show (1) that that type of structure which may well be called idiomorphic occurs in deposits of the three metals, copper, zinc and iron; (2) that it occurs in them when they are formed during the prevalence of certain conditions of deposition common to the three cases; and (3) that it occurs in them because these conditions obtain.

Nomenclature.

The terms idiomorphic and hyp-idiomorphic, employed to denote the types of structure considered here, are used advisedly. They are borrowed from the vocabulary of the petrologist for two reasons: (1) There does not appear to the author to be any justification for the invention of new terms of description when such already exist as are amply sufficient, and (2) the terms idiomorphic and hyp-idiomorphic, used of structures in rocks, not

[1] Manuscript received February 1, 1922.
[2] Electrometallurgist, London, England.

only are fitly applicable to similar structures found in deposited metals, but are fitly appropriate on account of certain similarities between the modes of formation of igneous rocks, on the one hand, and electro-deposited metals, on the other.

By idiomorphic structure is meant the structure which results in a mass of rock or deposited metal when the crystals composing it have had the opportunity to develop their external forms freely.

By hyp-idiomorphic structure is meant the structure resulting from the fact that the component crystals (or the majority of them) have n o t had the opportunity to develop their faces and edges freely, but, owing to mutual interference, have been compelled to take their shapes from their surroundings.[3]

It is suggested that these definitions are sufficient for indicative and descriptive purposes, though they may not be as exact as might be.

Experimental.

The conditions under which the deposits considered in this paper were formed were:

(a) For COPPER[4]

Solution.....1.5 kg. $CuSO_4$, $5H_2O$; 200 cc. $HClO_4$ (sp. gr. 1.12); and 4.5 lit. water.
Current density...14 amp./sq. ft. (1.6 amp./dm.^{2}) at beginning.
E. M. F.....0.4 volt, at 6¼ cm. electrode distance.
Temperature.....ordinary.
Time .....(about) 3 days.

(b) For ZINC

Solution .....$ZnSO_4$, $7H_2O$. 1.75 N (for hydrated salt).
Current density...4.5 amp./dm^2. (40.5 amp./sq. ft.) at beginning.
E. M. F.....1.25 volt, at 3 cm. electrode distance.
Temperature .....ordinary.
Time .....3 hours.

(c) For IRON[5]

Solution .....$FeCl_2+CaCl_2$. The Fischer-Langbein bath,[6] made from $FeCl_3$ solution (sp. gr. 1,375, *i. e.* 56% $FeCl_3$) and 5 lb. $CaCl_2$, anhyd., to form 13.5 lit. (3 imperial gal.) of solution.

[3] The definitions are those given, in much the same wording, by A. Harker, Petrology for Students, 1895.

[4] W. E. Hughes, Idiomorphic Crystals of Electro-deposited Copper, Jour. Inst. Metals, 1920, 23, 526.

[5] W. E. Hughes, "The Forms of Electro-deposited Iron, and the effect of Acid upon its structure," Trans. Far. Soc., 1922, **17**, 442.

[6] D. R. P., No. 212, 994 (1908).

Current density...140 amp./sq. ft. (16 amp./dm^2., approx.) at beginning.
E. M. F.....0.7 volt, at 8.75 cm. electrode distance.
Temperature .....100°C.
Time .....The part considered was a portion of a 1.5 mm. thick deposit. The time occupied in the formation of the section in question is uncertain.

The cathodes were in all cases short cylindrical pieces of metal. It will be noticed that, in the cases of zinc and iron, the current density was very high for continuous "still vat" deposition, while, in that of copper, it was somewhat above the normal.

Discussion.

1. The first object of the present paper is to show that idiomorphic forms of copper, zinc and iron occur in deposits of these metals.

It is suggested that the micrographs show this quite clearly. The least definite are Figures 3 and 4, showing sections of zinc deposits. This indefiniteness is, however, due to the rounding of the edges and angles of the crystals situate on the surface of the deposit, and the rounding is, in turn, due, in some part, to the action of concentration currents during the formation of the deposit, but, in greater part, to defective polishing. Figure 3 shows well the peripheral outline of an idiomorphic crystal of deposited zinc—the projection on the plane of the paper of the prism faces and the pyramid end of the crystal. The brilliant facets of the multitude of terminal pyramids on the surface of the deposit caused this to appear like a glittering mass, even to the unaided eye; when the specimen was examined with a hand lens, the faces and the angles and edges, both often quite sharp, of the crystals could be easily distinguished.

2. The second object is to show that idiomorphic forms of copper, zinc and iron are formed under like conditions of deposition.

The expression just used is not intended to convey the meaning that the individual factors that may affect the structure of a deposit (factors such as concentration of electrolyte, current density, temperature and so on) are the same in the cases of the three metals, copper, zinc and iron when idiomorphic crystals are

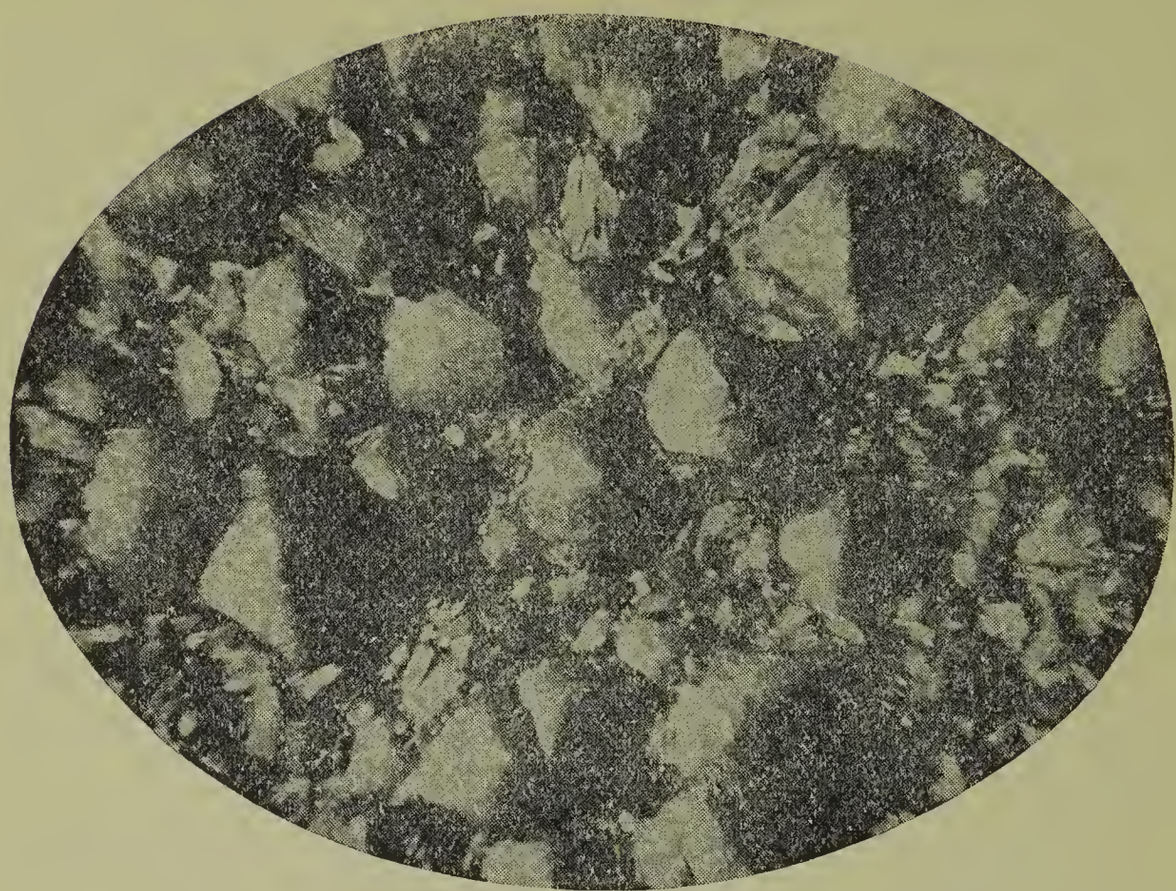


FIG. 1. x 20
(Idiomorphic Crystals; Oblique Illumination)

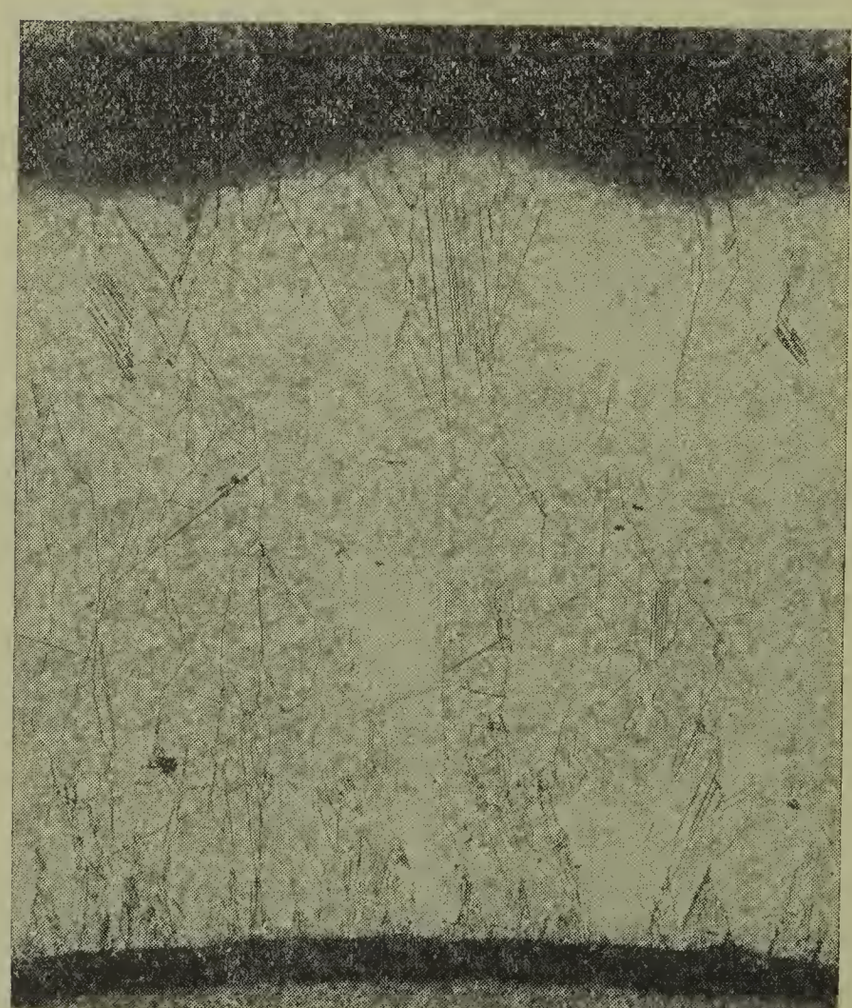


FIG. 2. x 50
Interior Structure of Deposit having idiomorphic structure shown in Fig. 1. Etching reagent; 0.880 Ammonia.

ELECTROLYTIC COPPER

formed. What is meant is that the resultant conditions of things, occasioned as the algebraic sum, so to say, of the factors operating, is the same in the three cases. This resultant condition is, in the case of the formation of idiomorphs of deposited metals expressed as low concentration of free and available metal atoms in the cathode neighborhood.[7]

(a) *Copper.* The case of copper has been considered elsewhere.[8] It was there shown that the factors of deposition were such as would result in very low concentration of available metal atoms in the cathode neighborhood, and it was urged that, on the analogy of the known facts in regard to the crystallization of salts from solutions, this low concentration could be considered as the cause of the formation of the idiomorphic crystals.

(b) *Zinc.* If the factors of deposition that operated during the formation of the zinc deposit be considered, it will be seen that their resultant, too, is low metal concentration in the neighborhood of the cathode. The current density employed being very high (for "still vat" work), the cathode layer of solution must soon have become low in metal concentration, because such factors as would supply that layer with new metal are either absent or insufficient.

These factors are (1) mechanical movement of the electrolyte or the cathode; (2) heat convection currents; (3) ion migration; (4) liquid diffusion; (5) movement due to gas evolution at the cathode; and (6) concentration currents. The first was definitely absent. So, practically, was the second: the total rise of temperature during the whole period of deposition (3 hours) was only 3°C., the final temperature being 24.5°C. The third and fourth factors cannot be conceived as being of any importance for the purpose of maintaining the supply of metal in the cathode layer of solution. There remain only the fifth and sixth factors, namely, movement due to evolution of gas and concentration currents. As regards the former, the observations made during the period of deposition show that this factor was, in the present instance,

[7] W. E. Hughes, "Electro-deposition of Iron," pubd. by The Stationery Office, London, for the Dept. of Scientific and Industrial Research, March, 1922.

[8] Jour. Inst. Metals, *loc. cit.* Descriptions of idiomorphs of deposited copper—from the crystallographic point of view—have been given by G. von Rath, Sitzungsber, der Niederrheim, Ges., Bonn, 1887, 283, and by O. Mügge, Verh. d. nat. Ver. Rheinl. Westf., 1889, (5), 6, 96.

FIG. 3. x 175
Idiomorphic Crystal of Zinc
The crystal shows slip lines on right hand side.
Etching reagent: 1% nitric acid in water.

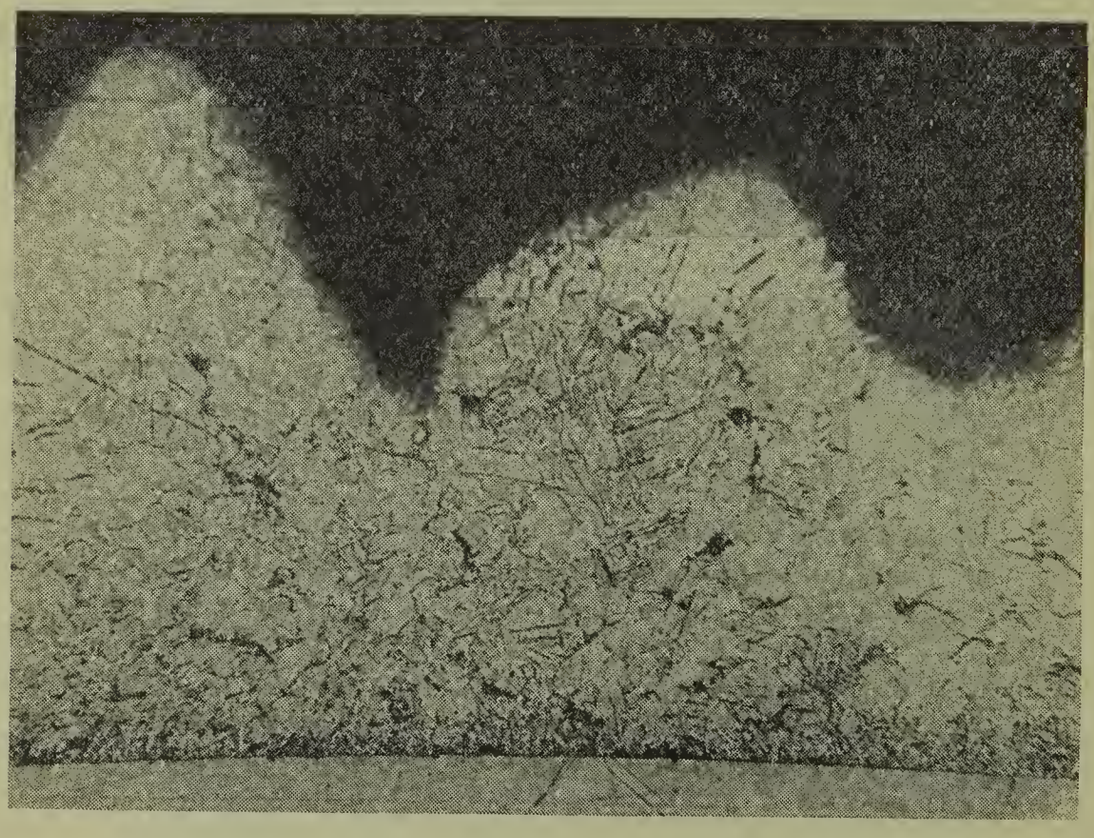


FIG. 4. x 150
Section of deposit showing idiomorphic surface and hyp-idiomorphic structure below. The angles of the crystals are rounded, but their general crystallographic form is clear.

ELECTROLYTIC ZINC.

ineffective. The deposition commenced at 11.40 a. m. Shortly afterwards the record was made: "No cathode gas bubbles visible." At 12.10 the following note was made: "No gas visible; none evolved on tapping cathode." And at 2.20 it was recorded: "One or two bubbles on tapping cathode."

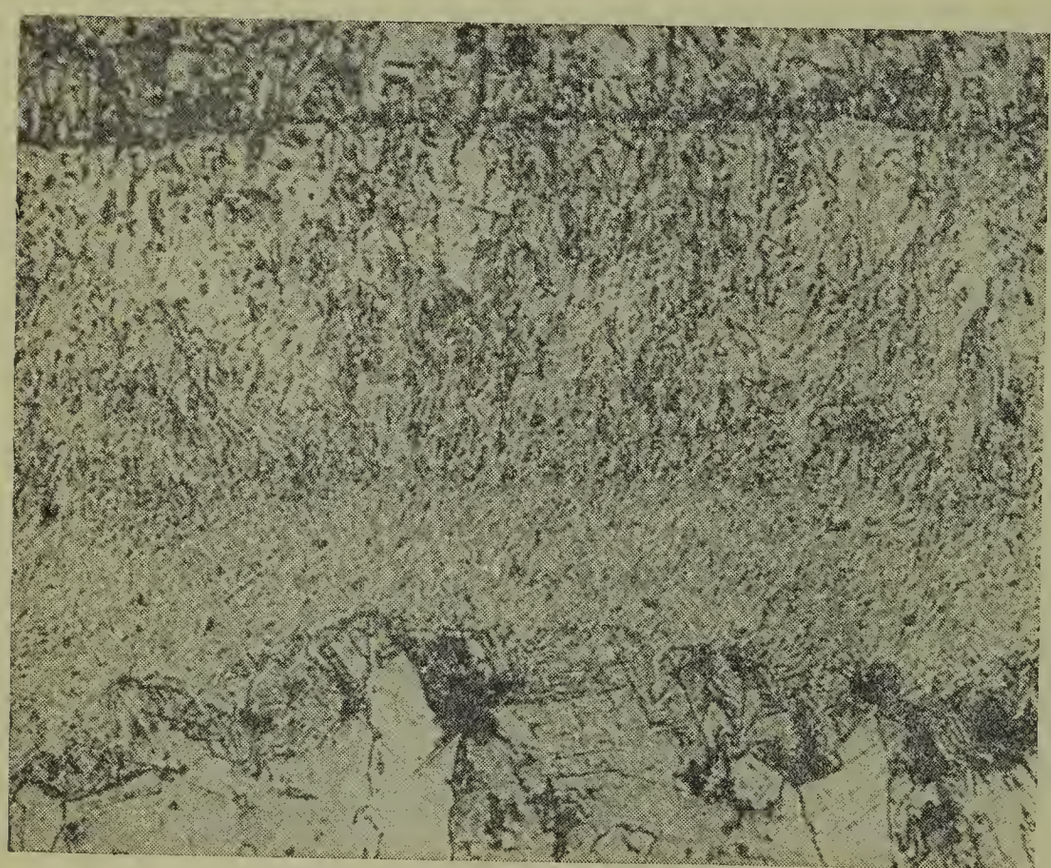
While, therefore, it is true that evolution of gas has been considered by R. Kremann and H. Breymesser[9] capable of giving rise to a stirring movement sufficient to affect the structure of the deposit, the amount of gas evolved in the present case, and its rate of evolution, were, undoubtedly, far too small to give rise to any such movement. Moreover, the effect of gas evolution upon the structure is, in the view of these authors, to diminish the size of grains of which the deposit consists, because, they say, "large crystals are formed when growth is undisturbed." There remains, therefore, only the effect due to concentration currents.

Anyone who has closely watched the visible phenomena at the cathode during deposition is aware of concentration currents. They leave their mark upon the deposit itself. Grooves parallel to the axis, or spiral, on the surface of a deposit on, say, a cylindrical cathode, are due to them; so, too, are the spoon-shaped depressions that represent shadows, so to say, on the deposit of bubbles of gas resting on it. The former defect is often referred to, in plating-shop language, as "current marks," though the plater's use of the word "current" is, wrongly, connected with the "electric current." One has to remember that, unless by means of concentration currents, it is not easy to understand how continued deposition of metal could occur in "still vat" work, for there is no other obvious means whereby ions could quickly enough reach the cathode.

Concentration currents must, therefore, operate to replenish the cathode layer of solution with new metal; but that they are at all sufficient to maintain anything approaching constancy of metal concentration there is not at all likely. Indeed, observation alone is enough to show that supply due to concentration currents must be small. The currents can be seen to rise along the surface of the cathode, the upper surface of which must, therefore, be always contiguous with solution that is, to a great

[9] Monatsh, f. Chemie, 1917, 38, 359.

FIG. 5. x 1,000
Idiomorphic Crystal of Iron
The crystal shows etch figures resulting from deep etching with 3 percent HNO_3 in abs. alcohol.



Fibrous (below) growing into normal structure as bath becomes less acid and finally neutral.

Fibrous structure due to acid.

Layer of idiomorphic crystals with hyp-idiomorphic structure below.

FIG. 6. x 300
Internal structure of deposit shown in fig. 5.
ELECTROLYTIC IRON

extent, exhausted of metal. This deprivation will, indeed, be all the greater and all the more continuous because of the actions of concentration currents, as the following considerations show. The current density was greatest at the bottom end of the cylinder on which the zinc deposit was formed, as it always is at the end, edges and corners of any cathode. Here, therefore, the solution soonest becomes deprived of its metal to a great extent. Hither the inflow of metal-laden solution occurred, and hence the metal-exhausted solution outflowed upwards over the surface of the cathode.

The high current density used operated continuously to deprive this new solution of the greater part of its metal content, and, at the same time, to thicken the deposit around the bottom edge of the cathode. The combined, accumulating, effect of concentration currents and high current density was to give occasion for the final record regarding the deposit: "Outgrowth—quasi cindery." But as the deposit thickened and became more and more dendritic around the bottom edge of the cathode, the more the discharge of ions would become localized there,[10] and the more effectively would the outflowing concentration currents operate in carrying upwards over the cathode's surface solution weak in metal.

Hence, although the concentration currents do, undoubtedly, operate to maintain metal in the cathode layer of solution, yet they do so only to a very small extent, in so far as the general surface of the cathode is concerned; and, indeed, they must operate to maintain that metal concentration at a low value, which is the condition favorable to formation of idiomorphs. The zinc deposit was, therefore, formed under a resultant condition—low metal concentration—similar to that in which the copper deposit was formed.

(c) *Iron.* In the case of the iron, the layer of idiomorphic crystals was, finally, located within the deposit. It was formed during a time in which the deposition process was not interfered with. Preceding the time of its formation, additions were no longer being made to the solution;[11] this gradually became neutral, and a gradual change of structure occurred from fibrous to normal.

[10] O. Lehmann, Zeit. f. Krystallographie, 1890, **17**, 274.
[11] Trans. Far. Soc., *loc. cit.*

This latter developed into hyp-idiomorphic structure, which, in turn, developed into the idiomorphic. The current density was maintained very high (at, namely, 140 amp./sq. ft.). The temperature was approximately constant,[12] so that heat convection currents were slight. There was no mechanical movement; and movement due to gas evolution was observed to be very slight. What has been said above as to the operation of concentration currents applies to the case of the iron with more, and not less, force, because of the higher current density. In this case, also, therefore, the resultant condition—low metal concentration in the cathode layer of solution—obtained, just as in the cases of the copper and zinc deposits already considered.

3. The third object of this paper is to show that idiomorphs are formed because of the prevalence of the resultant condition defined above.

It may be recalled that the process of the formation of electro-deposited metal is, almost universally, regarded as a crystallization process. The evidence in favor of this view is abundant and convincing; and it is the view expressed by all those workers who have seriously investigated the matter.[13] Not only is this so in the cases of deposits which, like those being considered, show actual crystals, possessing angles, edges and faces of great reticular density, but it is also the case where, at first sight, crystalline structure is not so obvious.

In such cases, one can frequently observe slip-lines[14] and etch figures in suitably polished and etched samples; these appearances are inconsistent with the amorphous condition. This being so, it is only to be expected that conditions which give rise to this or that form in the cases of other crystalline substances will occasion the development of similar forms in the case of deposited metal. O. Lehmann states that he could find no other reason to explain certain facts connected with the electro-deposition of metals than that the same laws govern the crystallization of both

[12] A piece of asbestos board interposed between the wrought iron containing tank and the source of heat—a gas-ring burner.

[13] E. g. O. Lehmann, op. cit.; F. Foerster, Elektrochemie wäss. Lösungen, 1915, p. 328; A. H. W. Aten & L. M. Boerlage, Rec. Trav. Chim. Pays-Bas, 1920 **39**, 720; and many others.

[14] Observed by O. Faust, Zeit. f. anorg. Ch., 1912, **78**, 201, and others in electrolytic copper, and by the author (Jour. Iron & Steel Inst., 1921, **103**, 355) in deposited iron.

deposited metals and salts.[15] Among such conditions are the labile and metastable states of the solutions from which salts are formed. From a solution in the labile condition, either very small crystals or dendrites are deposited. Lehmann (*op. cit.*) has shown that dendrites or skeleton crystals of tin are formed from stannous chloride solution as the result of quick separation of metal and its consequences, similarly as "in the case of ordinary crystallization, increase in the velocity of separation causes the external form (of a crystal) to be destroyed in favor of the formation of skeletons, which are branched the more finely, the greater the velocity of growth becomes." [16]

Such a condition as exists in the solution when the electro-deposition is proceeding at a fast rate will certainly be labile; it will approximate to the condition of a highly supersaturated salt solution. On the other hand, the metastable condition will exist when the available metal concentration is low. On analogy with salt solutions, one may expect to get a finely crystalline or dendritic deposit in the former case, and a coarsely crystalline or idiomorphic deposit in the latter. In fact, these expectations are realized; and the conclusion seems justified, therefore, that it is because of the existence of the condition of low metal concentration that idiomorphic forms are obtained.

The correlation of macroscopic aspect and internal structure.

Briefly, the hyp-idiomorphic structure is that within the mass of deposited metal which corresponds with an idiomorphic structure on the surface. The former grows into, or becomes, the latter as deposition continually proceeds. The relation is analogous to that obtaining between normal within and coarsely crystalline on the surface, or, again, between fibrous within and very finely crystalline, or, apparently, amorphous, on the surface. The general relations between these various types of structure can be put thus—

Fibrous	→	normal	→	hyp-idiomorphic	. . within.
⇃↾		⇃↾		⇃↾	
Finely crystalline	→	coarsely crystalline	→	idiomorphic	. . surface.

[15] *op. cit.*

[16] A. E. Tutton, "Crystals", 1911, figs. 99 and 100.

These relationships are of importance in the workshop. It is recognized that many of the mechanical and physical properties of a metal depend upon its structure. A knowledge of this is, therefore, of importance to the plater no less than to the metallurgist. Knowledge of the relationships set out above will enable the plater, by watching the deposit during its formation, to know what its internal structure is. It will enable him to maintain better control over his processes and products. But a word of caution is necessary. If deposition is commenced and allowed to continue for a considerable period, say, three hours, and only the final surface of the deposit noted, deductions as to internal structure, drawn from that inspection, may be wrong. And for this reason, if the conditions of deposition vary, so, too, will the structure of the deposit. These conditions will, almost surely, vary in the majority of cases of "still vat" deposition; hence, the structure of the deposit also will vary.

For instance, a bath containing free acid will, usually, become less and less acid as deposition continuously proceeds. Now, the effect of the presence of free acid in a solution is to cause the structure to be fibrous. This is undoubtedly so in the case of iron, deposited from the ferrous calcium chloride bath,[17] and in that of zinc, deposited from solutions containing sulphate of zinc and free sulphuric acid.[18] As the amount of free acid becomes less and less and the bath becomes neutral, so the structure changes from finely fibrous to coarsely fibrous and, then, to normal.[17]

Another instance of common occurrence may be noted. Where a bath is agitated or rod movement is employed, a marked change is noticeable in the structure of the deposit as a result of cessation of the agitation or movement.[19] If, then, agitation or movement be interrupted for any reason, and then, after a while, re-continued, the deposit formed during the rest period will be markedly different in structure from the deposit formed before and after the break, which will be, *ceteris paribus*, the same. The result in this case is that the structure of the deposit, considered as a whole, is not homogeneous.

Examination of the final surface tells one only what the internal

[17] Trans. Far. Soc., *loc. cit.*

[18] As shown by unpublished work of the author.

[19] W. E. Hughes, "Electro-deposition of Iron", *loc. cit.*

structure of the outer portion of the deposit is. But, if the surface of the deposit be observed at frequent intervals, and if the conditions are known that will give a deposit of homogeneous structure of this or that type, then, by such observation, one will know when the conditions are varying (for instance, whether and when it is necessary to add more acid to the solution), and hence maintain good control. The eye soon becomes able to detect even slight differences in the macroscopic aspect of a deposit, as, for instance, whether the crystalline aspect is becoming finer or coarser, or, again, a change from (apparently) non-crystalline to minutely crystalline.

Summary.

1. Idiomorphic and hyp-idiomorphic structures in electro-deposited copper, zinc and iron are shown in photomicrographs.

2. The resultant condition of deposition under which such structures are obtained is described. This is defined as low concentration of free and available metal atoms in the cathode neighborhood.

3. An attempt is made to show that the structures considered are formed because of the existence of that resultant condition.

4. Macro-structures and micro-structures of deposited metal are correlated, and the importance of a knowledge of that correlation in workshop practice is pointed out.

The author wishes in this place to recognize generally his indebtedness to many of the pioneers who worked on the electro-deposition of metals, and whose publications are, not unusually, passed over nowadays. His ideas are undoubtedly influenced by their work, but in such a way that it is difficult, usually, to acknowledge specific instances. The author can, however, state that his endeavor to take a broader view of the phenomena of the formation of deposited metals was certainly instigated by much of Professor C. F. Burgess' work, and especially by the paper entitled "Structure of Electro-Deposits," by Professor Burgess and O. P. Watts,[20] and he has pleasure in expressing his indebtedness thereto.

[20] Trans. Am. Electrochem. Soc., 1906, 9, 229.

DISCUSSION.

WM. BLUM[1]: I am going to discuss the paper not so much from the standpoint of the subject matter, but from one point which will no doubt be referred to by the Publication Committee in the rules or directions which were suggested and would be helpful; that is, again referring to methods of expressing concentration of solutions. I will just call attention to the fact that the author has for his three equivalent solutions, that is solutions in which he is making comparable experiments, expressed the concentration in three different systems which are not exactly comparable with one another, and only one of which is strictly definite and reproducible. In one case he has given the amount of solids dissolved in a definite volume of water, and in another case the normality and in the third place he has given the specific gravity results in a solution on mixing two constituents together, but without stating the exact proportions in which they were mixed. The point is not with special reference to this paper and I would not want it taken in that connection, but rather to emphasize the fact that in this work on solutions, whether it is an electrodeposition or other comparable subject that it is important to define, in the first place, very specifically, the conditions used and preferably to define them in terms which will be strictly comparable, and which will permit the ready application of analytical data in connection with the control of such solutions. This point is not so much with respect to the subject matter of the paper, but rather using it as an unfortunate illustration of a principle which is sometimes overlooked.

M. R. THOMPSON[2] (*Communicated*): Mr. Hughes, if correctly understood, uses the terms, "fibrous," "hyp-idiomorphic," to denote relatively finely-crystalline structures, while the terms "normal" "idiomorphic," denote relatively coarsely-crystalline structures, in either case wherever the structure is found, as the location within or at the surface of a deposit is not taken to change the definitions.

It is stated on page 325 that "They (concentration currents)

[1] Chemist, Bureau of Standards, Washington, D. C.
[2] Chemist, Bureau of Standards, Washington, D. C.

must operate to maintain that metal concentration at a low value, which is the condition favorable to the formation of idiomorphs." Also, on page 327, "It is because of the existence of low metal concentration that idiomorphic forms are obtained." By "metal concentration," we understand metal ion concentration to be meant, since we are concerned with sulphate or chloride solutions in which the metal ion concentration has a more or less direct connection with the metal concentration, although not proportional to it in the strong solutions employed. (With cyanide solutions, of course, we always have a very low metal ion concentration, which may be associated with either a high or a low metal concentration). The conclusion to be drawn here is that decreasing the metal ion concentration tends to increase the crystal size, or to favor relatively coarsely-crystalline structures.

Now this conclusion apparently disagrees with Bancroft's commonly accepted third axiom of electrodeposition, in which it is stated that; "Increasing the potential difference at the cathode (decreasing the metal ion concentration), decreases the size of the crystals."[3] Further comment on this point would be of interest.

It is interesting to note that Mr. Hughes has found acidity to have a similar (probably primary) effect on iron deposits to that we have reported in the case of nickel deposits.[4] On page 325, he states; "This (the iron solution) gradually became neutral, and a gradual change of structure occurred from fibrous to normal," that is, decreasing the hydrogen ion concentration caused the deposit to become relatively more coarsely-crystalline. We understand the effect here to have been attributed entirely to hydrogen ion concentration and not to conditions of metal ion concentration, or current density. Of course, changes of hydrogen ion concentration capable of causing a very marked effect on the structure of iron or nickel deposits are not usually great enough to be regarded as materially affecting the metal ion concentration; there are good grounds for assuming a primary effect of hydrogen ion concentration upon structure of deposit (apparently a dispersion of the metal).

[3] Factors governing the structure of electrodeposited metals, Trans. Am. Electrochem. Soc., 1919, 36, 213.

[4] The acidity of nickel depositing solutions, Trans. Am. Electrochem. Soc., 1922, 41.

W. E. Hughes (*Communicated*): Mr. Thompson's critical remarks on my paper are both interesting and helpful to me. Possibly I have not made my meaning of the term "hyp-idiomorphic" clear to him. This term is not used to "denote relatively fine-crystalline structures." It denotes, as I use it, that structure which exists within a body of deposited metal which appears idiomorphic on its surface. A reference to the scheme set out on page 327 will show this.

Mr. Thompson suggests that the conclusion that decreasing the metal ion concentration favors coarsely crystalline structures "apparently disagrees with Bancroft's commonly accepted third axiom." The use of the term "axiom" as applied to the facts of electrodeposition does not appeal to me as a good one. I have stated the experimental facts as I have found them; and these facts show that coarse-grained structures and idiomorphs are formed in circumstances where a condition of low metal (ion) concentration must obtain. If Professor Bancroft has found, as an experimental fact, that decreasing the metal ion concentration decreases the size of the crystals, then this result is diametrically the opposite to mine. I have found the same result to occur in the cases of three metals, namely, iron, zinc, and copper. This fact seems to me to point to a truth of general application, as regards deposited metal, and, as I believe, aligns that metal alongside of other cases of crystalizing substances, whether ordinary metals, rocks, or salts. All of this confirms the view first put forward by O. Lehmann. I do not wish to say more on this matter here; I am returning to it in a later paper.

Mr. Thompson mentions also the fact that I have found that the presence of free acid causes an iron deposit, formed in the particular chloride bath I employed, to be of fibrous structure. That is a fact I carefully avoided attempting any explanation of in the present paper, in which I am not directly concerned with the fibrous structure. I am returning to that later also. Meanwhile, I am obliged to Mr. Thompson for reminding me of his experience with nickel, and I note the explanation he offers.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

THE ACIDITY OF NICKEL DEPOSITING SOLUTIONS.[1]

By M. R. Thompson[2]

Abstract.

The colorimetric drop-ratio method of measuring the pH, or hydrogen ion concentration, is applied by the author to nickel solutions. The acidity characteristics of various types of nickel depositing solutions are described. The relation between pH and cathode current efficiency is determined. The effects of pH upon the structure and properties of the deposited nickel are illustrated.

I. INTRODUCTION.

Although it has been long recognized that nickel deposition can be conducted successfully only within certain limits of acidity, there have been few attempts to measure or define these limits. The need for a "simple, rapid and convenient method . . . for determining the amount of . . . free acid in the nickel bath" was emphasized by Geo. B. Hogaboom, in 1916, in a paper upon "Some Unsolved Problems of the Electroplater."[3] The present work was conducted in the effort to develop such a procedure. It is believed that the approximate measurement of the hydrogen ion concentration by simple methods here described will furnish the most reliable means of defining the acidity characteristics of these solutions.

The actual reactions of nickel baths are very complex, and involve effects produced by many factors, including the composition and behavior of the anodes, and the presence in the solutions of dissolved or suspended impurities. Any thorough study of the

[1] Published by permission of the Director, Bureau of Standards. Manuscript received March 16, 1922.

[2] Chemist, Bureau of Standards, Washington, D. C.

[3] Trans. Am. Electrochem. Soc., 1916, 29, 371.

effects of hydrogen ion concentration must take into account these other variables, as their effects may be superimposed upon or even entirely mask those due to acidity. It has not been possible to conduct any such exhaustive investigation, and this paper is therefore offered primarily for the purpose of urging the measurement and recording of the acidity, both in commercial and experimental nickel deposition. If some satisfactory method is applied, another useful constant will have been standardized, it will be possible to draw more definite conclusions, and the results of different investigators can be more readily compared. The expressions, "slightly acid," "nearly neutral," etc., or references to the use of various test papers, as frequently encountered in the older literature on the subject, may then become obsolete and in their places will be found definite and reproducible values.

Any suggestions in this paper regarding the favorable range of acidity are purely tentative, and are advanced for the purpose of indicating to platers and chemists the probable limits of variation. Only after extended observations upon pure and contaminated nickel solutions, and with varied classes of plating, can definite operating directions be devised. In any given case these may require modification to meet special needs.

II. GENERAL PRINCIPLES.

The importance of controlling the acidity in nickel solutions is evident from a consideration of the relative positions of nickel and hydrogen in the electrochemical potential series, in which nickel is about 0.2 volt more electronegative or less "noble" than hydrogen. From this relation we can predict that on the electrolysis of a hypothetical solution which is normal both in nickel and hydrogen ions, only hydrogen would be deposited at the cathode unless the cathode potential were increased very much above the discharge potential for hydrogen. If, however, we decrease the hydrogen ion concentration (lower the cathode potential of hydrogen) or increase the nickel ion concentration (raise the cathode potential of nickel) it is obvious that we will bring the two potentials closer together, making it more difficult for hydrogen ions and easier for nickel ions to deposit at the cathode.

The relative cathode current efficiencies for nickel and hydrogen

could be calculated approximately from measurements of the single potentials of nickel and hydrogen in the solution, if it were not for the interference of at least two disturbing factors: (a) the overvoltage of hydrogen on nickel, and (b) the retarded deposition of nickel, which is usually attributed to a so-called "reaction resistance." This probably arises from a slow rate of discharge of nickel ions.

It is largely the first factor that permits the deposition of appreciable amounts of nickel at relatively high concentrations of hydrogen ions, although the quality of the nickel so deposited may be very poor. The combined and uncertain effects of the two factors make it impossible as yet to calculate relative current efficiencies from single potentials. Such efficiencies must therefore be obtained from direct measurements. In practical plating solutions the concentration of the nickel is seldom above 2 *N*, and that of nickel ions is probably of the order of magnitude of 0.1 to 0.2 *N*. Measurements made in such solutions indicate that the current efficiency of nickel deposition will approach 100 percent, *i. e.*, no large amounts of hydrogen will be evolved, at room temperature and with cathode current densities from 0.2 to 2 amp./ dm^2 (1.9 to 18.6 amp./ sq. ft.), if the concentration of hydrogen ions is kept within the limits of about 1×10^{-5} and 2×10^{-7} *N*, (pH, 5.0 to 6.7). The range of hydrogen ion concentration stated is somewhat wide and the best quality of plating deposit is usually obtained in a more restricted range, as will be discussed later.

III. METHODS OF EXPRESSING HYDROGEN ION CONCENTRATION.

This factor may be expressed in several ways, illustrated by the following examples for the same quantity.

1. $\frac{1}{100{,}000}$ *N*.
2. 0.000,01 *N*.
3. 1×10^{-5} *N*.
4. pH 5.0

The first method involves the inconvenience of awkward fractions; the second that of very small decimal quantities; the third

gives a ready idea of the relative quantities involved; the fourth, proposed by Sörensen, is most convenient and is rapidly gaining in popularity. The expression "pH" involves the logarithm of the reciprocal of the hydrogen ion concentration. It follows directly from the well-known equation of Nernst for the observed potential of the "gas chain," made by joining two hydrogen electrodes having unlike hydrogen ion concentrations, C and C.′

$$E = 0.0058 \log \frac{C}{C'}$$

If C is equal to normal hydrogen ion concentration, the equation becomes:

$$E = 0.058 \log \frac{1}{C'} = 0.058 \text{ pH}.$$

$\text{pH} = \log \frac{1}{C'}$, and becomes a convenient symbol for C′ itself. (The potential of a hydrogen electrode in a hypothetical solution normal in hydrogen ions is commonly used as the arbitrary zero of potential). The chief practical objection to the pH system is that a numerical increase in pH corresponds to a decrease in acidity and *vice versa.*

This use of larger numbers to express smaller quantities is analogous to the values used for wire and sheet metal gauges. At first it may cause confusion, but familiarity with the system can soon be acquired. For a discussion of the relation between these systems of expression, consult the recent text of W. M. Clark.[4] In this paper the pH notation will be used exclusively.

A careful distinction must be drawn between the amount of acid, or total acid concentration, and the hydrogen ion concentration, or degree of acidity. The distinction is just as important as in the parallel case of quantity of heat, and degree of heat or temperature. Solutions of 0.01 *N* hydrochloric acid and 0.01 *N* acetic acid contain equivalent amounts or concentrations of acid, as determined by titration with standard alkali (to appropriate end points), but the hydrogen ion concentration in the case of the strong acid (hydrochloric acid), will be about pH 2.0 (1×10^{-2} *N*), *i. e.,* we may assume practically complete dissociation, while the

[4] The Determination of Hydrogen Ions, Williams and Wilkins Co., Baltimore, 1920.

hydrogen ion concentration in the case of the weak acid, (acetic acid) will be about pH 3.5 (4×10^{-4} N). For most purposes in nickel deposition the pH, or degree of acidity, has the greater significance, although in order to secure or maintain a definite pH a knowledge of the acid content may be helpful.

IV. MEASUREMENT OF pH.

The primary method of measuring the pH of a solution depends upon the hydrogen electrode, by means of which the other secondary methods are standardized. Methods for using the hydrogen electrode are fully described by W. M. Clark in the text referred to above. The hydrogen electrode involves the use of somewhat delicate and expensive apparatus, and considerable experience is required before one can become expert in its use. It is therefore not well adapted for rapid, approximate measurements outside of the laboratory.

A secondary colorimetric method is available, involving the use of dyes, or indicators, whose constants have been determined by means of the hydrogen electrode. This method presents great advantages for research or commercial work, in which approximate results suffice. The indicator method as perfected in recent years by a number of investigators was therefore used by the author in the work described in this paper.

Expressed in its simplest terms, the color of an indicator in a solution varies with the degree of dissociation of the indicator, which in turn is a function of the hydrogen ion concentration of the solution. Methyl red, which has a dissociation constant of 10^{-5}, will be 50 percent dissociated in a solution of pH 5.0 and at 50 percent dissociation it exhibits a definite color at a given concentration. When, for example, the pH is 5.6, the dissociation will be approximately 20 percent, and another definite color will be exhibited. To use the indicator as a color standard, we therefore need either to produce a definitely known pH in its solution, or to secure a definite percentage dissociation of the indicator.

These principles are applied in the two following distinct methods of preparing indicator color standards.

1. The indicator is added to a solution of known composition and pH, of which the relation has been previously established by means of a hydrogen electrode. Solutions used for this purpose

usually contain weak acids or their salts, because such solutions are well "buffered", *i. e.,* they do not (in the appropriate range) change in pH rapidly when small amounts of acid or alkali are added to them. They therefore do not require very high precision in their preparation, and they are relatively stable when exposed to glass containers or to the atmosphere.

2. The drop-ratio method devised by L. J. Gillespie[5] is employed to secure a definite percentage dissociation of the indicator. If in each of two small tubes we dilute 5 drops of methyl red to 5 cc., and to one tube add a slight excess of alkali, and to the other an excess of acid, 50 percent of the original 10 drops of indicator is in the undissociated form and 50 percent in the dissociated form. By placing one tube behind the other and viewing the pair by transmitted light, we obtain the same optical effect as if the original 10 drops of indicator were all in a single tube and dissociated 50 percent. The resultant color with methyl red corresponds to the color of this indicator in a solution the pH of which is 5.0. A pair of tubes containing a total of 10 drops divided between them in the ratio of 4 alkaline to 6 acid represents 60 percent dissociation and the corresponding pH is 4.8. In this way methyl red is made to cover a range of pH 4 to 6, by means of eleven pairs of standard tubes, each pair differing by about 0.2 pH from the preceding pair.

If, as in the case of the green nickel solutions, the unknown solutions are themselves colored, their color after the addition of the indicator would not be directly comparable with the color standards. This difficulty is obviated by the method of G. S. Walpole,[6] which consists in placing back of the color standards a tube of the colored test solution, and thus compensating for the original color of the solution. Complete details of this procedure are available in the work of Clark previously mentioned. This method was used by the author for all the measurements reported in the present paper. The three indicators listed in Table I cover the maximum range of pH required for investigating or controlling nickel depositing solutions, and overlap sufficiently to confirm results at the extremes of their respective fields.

[5] Colorimetric Determination of Titration Curves without Buffer Mixtures, J. Am. Chem. Soc., 1920, **42**, 742.

[6] Chart Presentation on Recent Work on Indicators. Biochem. J., 1910, **5**, 207.

To prepare solutions of the sodium salts of these indicators, grind 0. 1 g. dry, powdered indicator in an agate mortar with the stated amount of 0.05 *N*. sodium hydroxide (1.1, 1.0 and 1.5 equivalents respectively); then dilute to 250 cc. with distilled water. This furnishes stock solutions containing 0.04 percent of the indicators, in the form of the monosodium salts. Apparently, standards prepared from the alcoholic solution of methyl red are more stable than those from the monosodium salt, therefore the former solution of this indicator is preferred. It may be prepared by grinding 0.1 g. indicator in a little 95 percent acid-free alcohol, diluting to 150 cc. with alcohol, and then with distilled water to a final volume of 250 cc. This furnishes a 0.02 percent (by volume) solution of indicator in 60 percent

TABLE I.

Range of Colorimetric Indicators.

Indicator	pH Range	CC. 0.05 *N* NaOH to dissolve 0.1 g. of indicator
Brom phenol blue	3.1 – 5.0	3.3
Methyl red	4.05 – 5.95	7.4
Brom cresol purple	5.3 – 7.2	5.6

(by volume) alcohol. Denatured alcohol will often suffice, but pure alcohol is preferable. Because of the green color of the nickel solutions, the concentrations of indicator solutions used are greater than those recommended by Gillespie.

The constants for the Gillespie[7] color standards are given in Table II. The volumes of acid or alkali required in each tube are indicated at the foot of the table.

To prepare the Gillespie color standards, it is convenient to use small thin-walled flat-bottomed "specimen tubes" of about 12.5 mm. (0.5 inch) outside diameter by 75 mm. (3 inches) in height. These may be marked with a file at a point corresponding to a volume of 5.5 cc. (5.2 cc. if alcoholic indicator solution is used.) The tubes selected for use should have a uniform bore. The tubes are set up in pairs in a rack, and the proper number of drops (a total of 10 per pair) of indicator solution and about 2 or 3 cc.

[7] *Loc. cit.*

of water are added to each tube. To the front tube of each pair is added the above specified volume of alkali, and to the back tube that of acid. The volume is then finally made up to 5.5 cc. (5.2 cc. if alcoholic solution of indicator is used), and the tubes are corked and shaken. The tubes having a ratio of 1.5 : 8.5 drops are prepared either by using 3 drops and 17 drops of indicator of half the usual strength, or else by diluting 3 drops and 17 drops of full strength indicator to final volumes of 11 cc. (10.4 cc. if alcoholic solution of indicator is used), and using sufficient of each solution to fill the respective tubes.

TABLE II.

Constants for Indicator Color Standards.

Drop Ratio		pH Number for Each Pair of Tubes		
Alkaline Tube	Acid Tube	Brom Phenol Blue	Methyl Red	Brom Cresol Purple
1	9	3.1	4.05	5.3
1.5	8.5	3.3	4.25	5.5
2	8	3.5	4.4	5.7
3	7	3.7	4.6	5.9
4	6	3.9	4.8	6.1
5	5	4.1	5.0	6.3
6	4	4.3	5.2	6.5
7	3	4.5	5.4	6.7
8	2	4.7	5.6	6.9
8.5	1.5	4.8	5.75	7.0
9	1	5.0	5.95	7.2
0.05 *N* HCl		1 cc	1 drop	1 drop
0.05 *N* NaOH		1 drop	1 "	1 "

To compare the color standards with a solution of unknown pH, it is convenient to use a small "comparator" or wooden colorimeter block, about 7.5 x 7.5 cm. x 6 cm. high (3 x 3 x 2½ in.) having nine vertical holes about 17 mm. (0.68 in.) in diameter, in three parallel rows (bored not quite all the way through the block). A diagram of a six-hole block is given by Gillespie. Through the face of the block, a horizontal hole, about 6 mm. (0.25 inch) in diameter is bored through each row of vertical holes, so that light may be transmitted through the tubes. The block is painted black, both inside and out.

When estimating the pH of a sample of nickel solution (which should be filtered if turbid), three spare tubes are placed in the front holes of the block, and 5 cc. of the nickel solution is pipetted into each. Ten drops of indicator are added to one tube and 10 drops of water to each of the others (4 drops of water if alcoholic indicator solution is being used). Two pairs of color standards are selected, judged to be near in color to the solution of unknown pH, and inserted in the block as shown in Table III. The standards are changed until two pairs are found having colors that lie on either side of the unknown, (or one of which matches the unknown). The pH of the sample can be estimated to 0.1 pH.

TABLE III.

Plan Diagram of Comparator Block.

Color Standard Tube (acid) 7	Water Tube 8	Color Standard Tube (acid) 9
Color Standard Tube (alk.) 4	Water Tube 5	Color Standard Tube (alk.) 6
5 cc. Nickel Solution + 10 drops Water 1	5 cc. Nickel Solution + 10 drops Indicator 2	5 cc. Nickel Solution + 10 drops Water 3

The two water tubes are used for better optical effect. The tubes are viewed through the holes in the front of the block, against diffused daylight, as secured from a northern sky, or through a piece of ground glass mounted in the window. Artificial light is unsatisfactory unless special arrangements are made.

The color standards will gradually alter or decompose, and should be freshly prepared two or three times a week. The stock solutions of the indicators are stable.

Some difficulty has been experienced in securing a uniform quality of brom cresol purple. Normally, the aqueous sodium salt solution has a permanent deep purple color. In case it assumes a reddish color on being first prepared, or turns reddish on standing, satisfactory results may not be obtained. Less

marked differences in color were secured with the different samples of brom cresol purple when the alcoholic solution was used, than with the sodium salt solution. Until manufacturers can furnish a uniform grade of indicator, the use of a 0.02 percent solution in 95 percent alcohol is preferable. All of the results recorded in this paper were secured with the sodium salt solution of one lot of the brom cresol purple of high quality.

It is common practice to control the acidity of a nickel solution by titrating a sample to some definite end point, *e. g.*, to the neutral color of sodium alizarin sulfonate,[8] which corresponds to about pH 5. Plating solutions are usually alkaline to this indicator, *i. e.*, have a pH above 5. The "alkalinity," thus determined, expressed in terms of cc. of 0.1 *N* alkali present in a given volume, is an indication of how much the solution differs from a fixed pH. If the "alkalinity" is kept adjusted within limits, the pH of the solution must remain between corresponding limits, although its exact value may not be established. This method may be entirely satisfactory for purposes of commercial control. As the results apply only to a given type of solution, it is not so useful in research work.

The use of methyl red for measuring and controlling the acidity of nickel solutions is not novel. In 1921, O. W. Storey[9] announced that for some time he had employed this indicator for that purpose, and had obtained very satisfactory results with it in a commercial plant. He did not make any pH measurements, but from his description of the colors secured, it appears probable that what he considered as "neutral" solutions (*i. e.*, suited for nickel plating) had a pH of 5 to 5.5. This experience of Storey shows that even the qualitative measurement of pH by an appropriate indicator may be very helpful in commercial practice. For comparison of results, however, definite numerical data are preferable.

V. CONTROL OF pH.

The maintenance of a uniform pH, or degree of acidity, in nickel solutions, depends primarily upon securing equal anode and cathode efficiencies. If the anode efficiency is less than the

[8] The use of this indicator was referred to by J. C. Andrews, Trans. Am. Electrochem. Soc., 1916, 29, 378.

[9] Monthly Review, Amer. Electroplaters' Soc., December, 1921.

cathode efficiency, the solution becomes more acid, *i. e.*, the pH decreases, and *vice versa*. Mechanical losses, such as are produced in all plating solutions by the removal of the cathodes, cannot of themselves cause any marked changes in acidity, as the pH of salt solutions, especially those containing weak acids, is not appreciably changed by even very considerable dilution. If, therefore, the pH of a nickel solution changes during operation, it is evident that there is a difference between anode and cathode current efficiencies, or that there has been accidental addition of acid or alkali to the bath, as through insufficient rinsing of the work being plated.

Under any given uniform conditions of operation there is a tendency for an equilibrium pH to be reached, the numerical value of which will depend upon such factors as the composition and temperature of the solution, the composition of the anodes and the areas and current densities of the anodes and cathodes. If by any means (as the addition of acid) the acidity is increased, anode corrosion will increase and cathode efficiency will decrease until this equilibrium is reached, and *vice versa*. Mere adjustment of the pH to any desired value will not insure uniform operation, unless other conditions are also properly controlled.

Measurement of the pH at regular intervals will indicate whether there is a tendency for change in acidity and, if such a tendency exists, the direction and extent of the change. Temporary remedies can then be applied, with increased assurance of getting the desired results, pending the selection of those conditions which will automatically maintain the desired pH.

The desired changes in pH can be made by the addition to the bath of appropriate acid or alkaline substances. To lower the pH, cautious additions of boric, hydrochloric or sulphuric acid are commonly made; to raise the pH, nickel or sodium hydroxides, or carbonates, or ammonia are employed. The choice of the reagent to be used must depend largely upon the type of solution, and be governed by the aim of avoiding the introduction of new metal or acid radicals into the solution (unless their presence is beneficial *per se*). Thus, ammonia should be used if the solution already contains ammonium sulphate or chloride, since the final equilibrium will be just about the same as if a

stronger base, such as sodium hydroxide, were added; and the latter would simply complicate the solution by the formation of sodium sulphate.

The approximate amount of any reagent to be added may be deduced from past experience, or from a "titration curve" of the particular solution in question (see Figs. 1 and 2 for typical

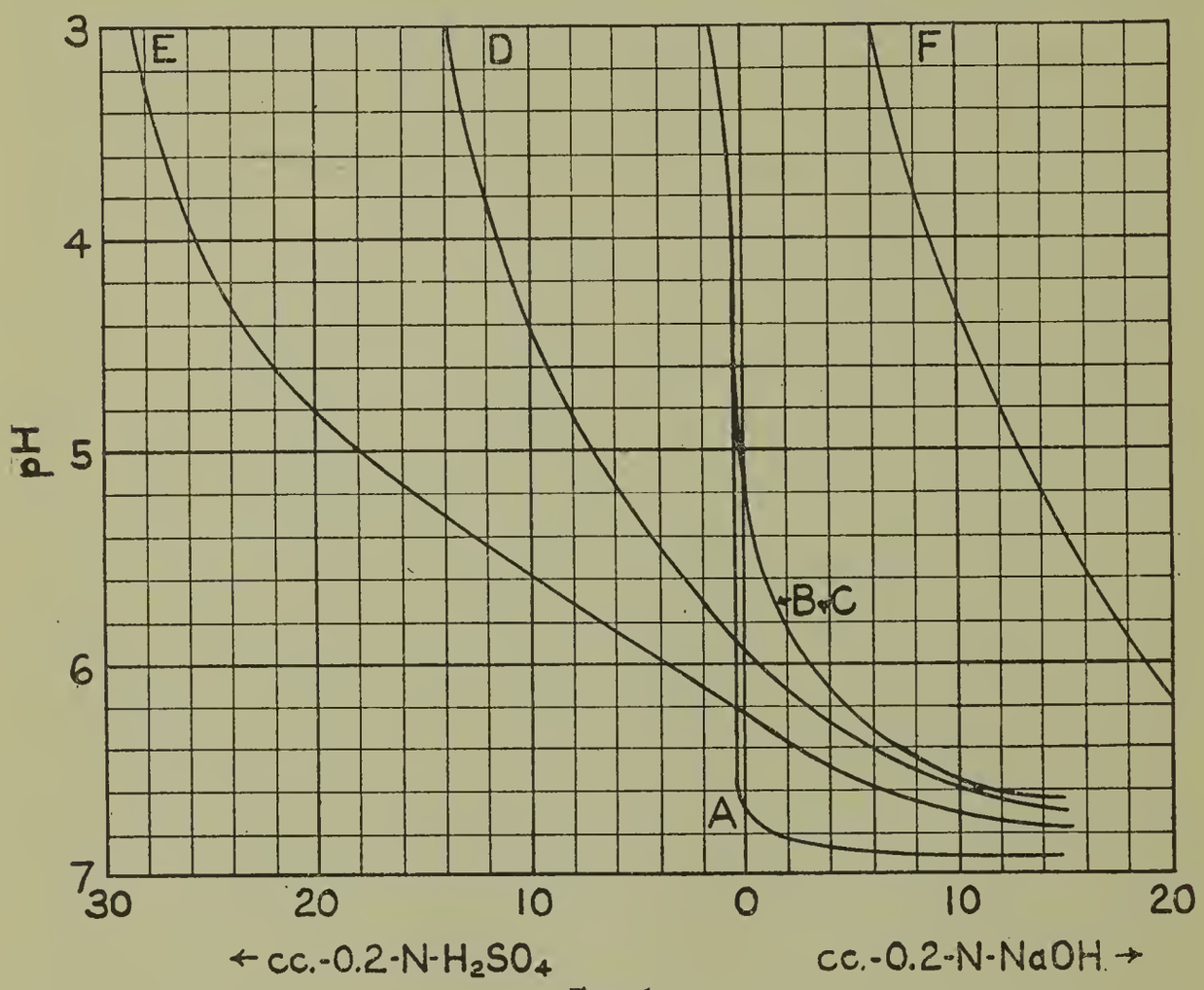


FIG. 1

Titration Curves for 50 cc of:

A—N $NiSO_4$
B—N $NiSO_4$; 0.5M H_3BO_3
C—N $NiSO_4$; 0.5M H_3BO_3 0.2N NaCl
D—N $NiSO_4$; 0.5M H_3BO_3; 0.1N NaF
E—N $NiSO_4$; 0.5M H_3BO_3; 0.2N NaF
F—N $NiSO_4$; 0.5M H_3BO_3; 0.1N HF

examples). These curves are constructed by adding standard acid or alkali solution to a measured volume of a filtered sample of the plating bath, observing the resulting pH at each step, and plotting the results. For control purposes it is not necessary to extend the curve to include the complete possible range of variation. From the observed and the desired pH of a bath at any time, and its volume, the weight of acid or alkali required

to bring about the necessary change in pH can be computed by reference to such curves. If large changes are involved the calculated addition is best made in several steps, checking up by measuring the result obtained each time. These adjustments should be made when the solution may be allowed to stand before use.

If, as previously noted, the pH of a nickel solution may be changed either by accidental or intentional additions to the bath, or by changes in operating conditions, such as anode and cathode current densities, it is important to know the rate of change in pH for any given change in conditions. For practical purposes we may assume that the effect of any process which influences the pH is equivalent to an addition of alkali or acid to the solution. Other things being equal, the best plating solution should be that in which the pH is least changed by a given addition of acid or alkali, as then if a desired pH is once secured it can be most readily maintained. Such a solution is said to be "well buffered." Hydrogen ion studies have shown that such solutions can be secured by having present in them weak acids or their salts.

One of the most common additions to nickel depositing solutions is boric acid, the function of which has been shown[10] to be that of maintaining a slight acidity in the nickel solution. Curves A and B (Fig. 1) show that between pH 3 and 6.5 a nickel sulphate solution is practically unbuffered, that is, a small addition of acid or alkali produces a great change in pH. The addition of boric acid flattens the slope of the curve very noticeably, especially toward the upper portion of this range (pH 5 to 6.5), and the solution is, therefore, much better "buffered." As in solutions containing only sodium salts boric acid does not show any appreciable buffer action below pH 7, its behavior in nickel solutions indicates that there probably exists in these solutions a certain amount of nickel borate, which influences the buffer action.

While the buffer effect of boric acid is very noticeable in the case of nickel sulphate (curves A and B, Fig. 1), it is just barely evident, if at all, in the case of nickel ammonium sulphate (curves

[10] L. D. Hammond, The Electrodeposition of Nickel, Trans. Am. Electrochem. Soc., 1916, 30, 103.

G and H, Fig. 2). It appears probable, therefore, that nickel borate does not exist in appreciable concentration in the presence of ammonium salts.

If fluorine, either in the form of hydrofluoric acid or a fluoride, is added to a solution containing boric acid, we then have present some complex and indefinite compounds generally referred to as "fluoboric acids" or "fluoborates." Whatever their constitution,

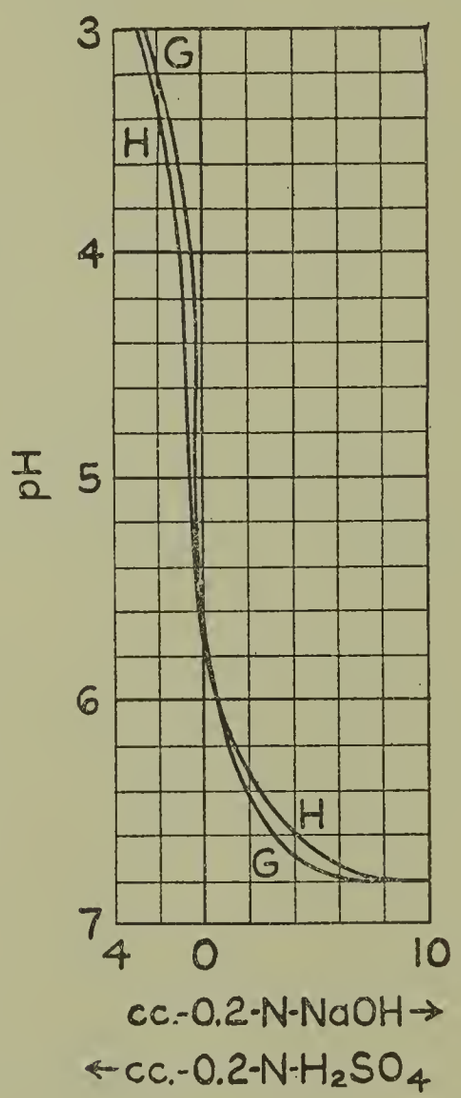


FIG. 2.

Titration Curves for 50 cc. of:
G—0.3*N* $NiSO_4.(NH_4)_2SO_4$
H—0.3*N* $NiSO_4.(NH_4)_2SO_4$; 0.3*M* H_3BO_3

such mixtures possess remarkable "buffer" action, which is roughly proportional to the amount of fluorine present, provided the boric acid is in excess. (Compare curves D, E, and F with curves A and B, Fig. 1.) Chlorides have no such effect (compare curve C), indicating that in these solutions at least, no complexes between chlorides and boric acid exist.

A nickel solution containing both fluorine and boric acid is, therefore, extremely well "buffered," and comparatively large additions of acid or alkali, or widely different anode and cathode current efficiencies, must occur to cause such a solution to change its pH rapidly. Whether this specific advantage of solutions containing fluorides is sufficient to justify their use under commercial conditions, must be determined by more extended practical experience with them than is now available.

Acetic, tartaric and citric acids are sometimes used in nickel plating baths. As they are also weak acids, although stronger than boric acid, it seems probable that they exert some "buffer" action in the solutions. No data concerning their effect on pH are available at present.

VI. EFFECT OF pH ON DEPOSITION.

(a) *Relation between pH and cathode current efficiency.*

The most obvious influence of pH upon the deposition is its effect upon the cathode efficiency, or, in other words, upon the relative proportions of nickel and hydrogen deposited under any given conditions. At first glance, it appears probable that certain difficulties encountered in nickel deposition, such as brittleness, curling, pitting, etc., may be directly connected with the acidity. Thus it is well known that deposited nickel shows a marked tendency for the absorption of hydrogen, and that the "alloy" so produced is decidedly brittle and tends to curl or crack. Similarly, it is recognized that in some cases at least, pitting is initiated by the presence of hydrogen bubbles on the cathode.

But, as previously indicated, there is abundant evidence that other factors, such as the presence of iron, copper or zinc, have a direct bearing upon the character of the deposit. Brittleness is often ascribed to the presence of iron. We may assume that all commercially operated nickel solutions contain iron, as, even if the solutions are initially pure, the anodes contain from 0.6 percent to as high as 5 percent of iron. In such solutions there is a tendency for the iron, which is dissolved as a ferrous salt, to oxidize, and in some cases to hydrolyze with the formation of basic ferric sulphate or borate.

Admitting then that the presence (and form) of iron in the solutions has an important bearing upon the character of the deposits, the control of pH is all the more important, as in any given solution the rate of oxidation and hydrolysis of the iron is influenced directly by the acidity. Similarly, the relative importance of various causes of pitting can be determined only if means are available for measuring and controlling the pH.

In order to secure preliminary information which would indicate at least the major effects of changes in pH under existing commercial conditions, experiments were conducted with commercial nickel salts and anodes, and the cathode efficiencies and marked characteristics of the deposits were noted. Observations were first made on a "chloride" solution and a "fluoride" solution, having the composition shown in Table IV.

TABLE IV.

Nickel Solutions.

Solution No.	1			2		
	N	g/L.	oz/gal.	*N*	g/L	oz./gal.
Nickel sulphate.	1.0	140	19	1.0	140	19
Boric acid.....	0.25M	16	2	0.25M	16	2
Sodium chloride	0.1	6	0.8	..	..	..
Sodium fluoride	..			0.1	4	0.5

Deposition was carried out under the following conditions: The solutions were operated at room temperature without agitation. Deposits were made upon steel plates to an approximate average thickness of 0.013 mm. (0.0005 inch), which required a current of 1 amp.hr./dm^2 (9.3 amp.-hr./sq. ft.). The anodes were commercial 95 to 97 percent cast anodes, covered with cotton bags to prevent particles being carried over to the cathode. The anode current density was approximately equal to the cathode current density. The pH was adjusted by the addition of sulphuric acid or sodium hydroxide, and was measured by the Gillespie drop ratio method, using brom phenol blue or brom cresol purple as indicators. The cathode current efficiencies were measured by means of a copper coulometer. These are

plotted in Fig. 3. Runs were also made at several current densities intermediate between 0.2 amp./dm² (1.9 amp/sq. ft.) and 1.5 amp./dm² (13.9 amp./sq. ft.). The curves for these results would lie between the respective limiting curves of low and high density, but are omitted for the sake of clearness.

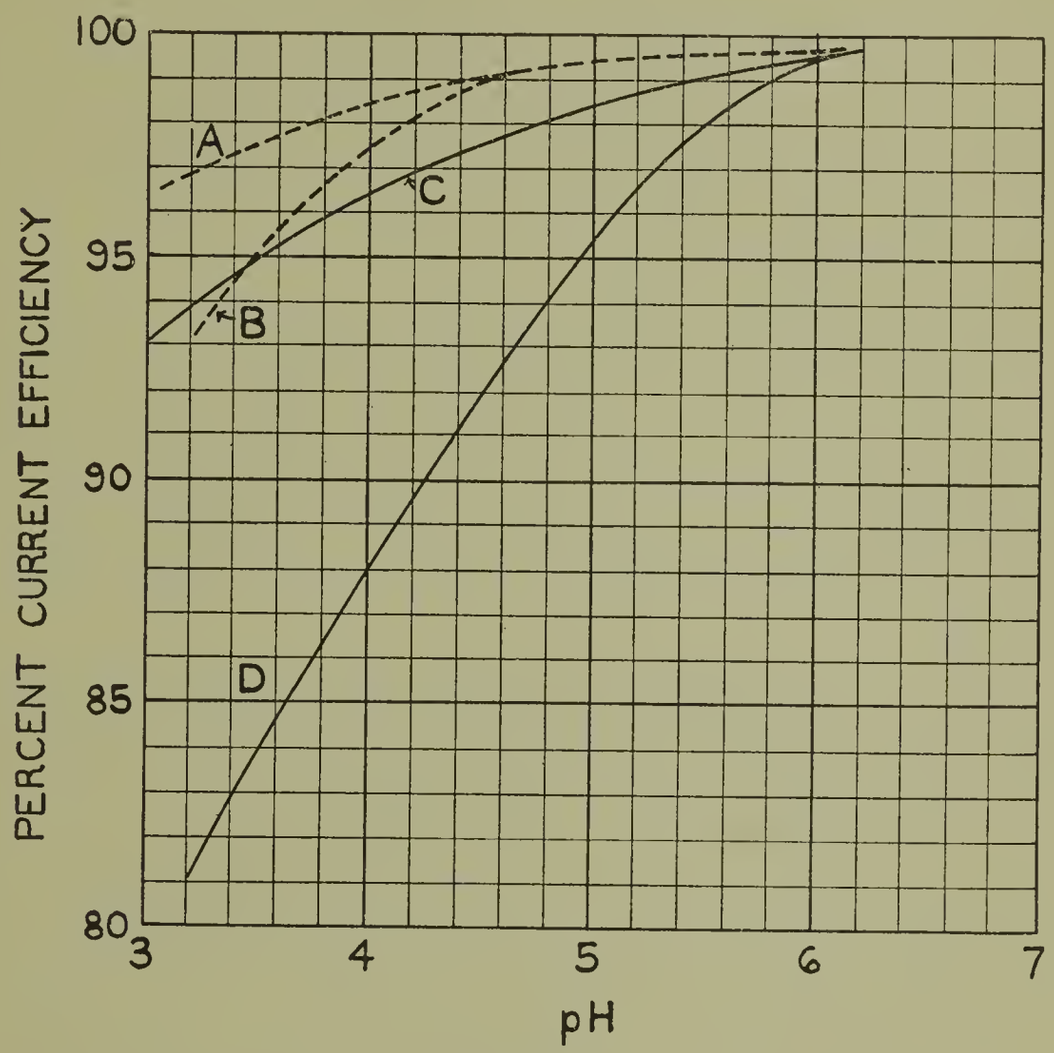


FIG. 3.
Cathode Efficiency of Nickel Deposits:
A—1.5 amp./dm² (13.9 amp./sq. ft.)
B—0.2 amp./dm² (1.9 amp./sq. ft.)
In N $NiSO_4$ 0.25M H_3BO_3;—0.1N NaCl
C—1.5 amp./dm² (13.9 amp./sq. ft.)
D—0.2 amp./dm² (1.9 amp./sq. ft.)
In N $NiSO_4$ 0.25 M H_3BO_3;—0.1N NaF

From Fig. 3, it may be seen that for constant current density, the cathode efficiency increases as the pH increases, approaching a maximum in the chloride solution at about pH 6. For a constant pH, the current efficiency increases as the current density is raised in the working range studied. At first this behavior appears anomalous, but consideration of the relative discharge potentials of nickel and hydrogen shows that in solutions con-

taining their ions, as the current density and, therefore, the cathode potential is increased, the proportion of nickel to hydrogen that is discharged must also increase. This increase in cathode efficiency with increased current density is characteristic in some degree of all metals above (more negative than) hydrogen, such as nickel, iron, zinc, etc., as distinguished from metals such as copper, silver, etc., in their acid solutions, where the current efficiency does not tend to increase with increased current density. Even with nickel and zinc, however, there is a limiting current density, dependent in part upon the degree of agitation, beyond which the efficiency decreases.

Another contributory cause for this increase in current efficiency with current density is that the overvoltage of hydrogen on nickel increases with the current density. The reaction resistance of the discharge of nickel ions tends to counteract the effect of overvoltage, *i. e.,* to reduce the cathode efficiency at high current density; and its effects may be even greater than the overvoltage.

At a low pH, especially at low current densities, the fluoride solution has a much lower cathode efficiency than has the chloride. At higher pH, and with high current densities the cathode efficiencies in both solutions are nearly 100 percent.

All of the pH measurements were made upon samples taken from the body of the solution. It is well known, however, that in still plating solutions there is a tendency for the layer of liquid next to the cathode (and also that next to the anode) to acquire a different composition than the body of the solution. This may be readily confirmed by observing the convection currents, usually upward at the cathode, and downward at the anode. With any cathode efficiency less than 100 percent, that is, when hydrogen ions are discharged, there must be a tendency for the layer of liquid adjacent to the cathode to become less acid.

This behavior was made the basis of the explanation of Bennett and his associates,[11] for the fact that in solutions to which ammonia had been added, the cathode efficiency was increased. They postulated as a condition for nickel deposition with high efficiency, the existence at the cathode of an "alkaline film."

[11] Bennett, Kenny and Dugliss. Electrodeposition of Nickel. Trans. Am. Electrochem. Soc., 1914, **25**, 335.

Probably in the light of the above discussion this may be better defined as "a film of minimum acidity," as in the strict sense it is impossible for a nickel sulphate solution to be alkaline, that is, have a pH above 7, owing to the precipitation of nickel hydroxide below that point. Bennett did not, however, make any actual pH measurements, and, therefore, it is difficult to correlate his results exactly with those here reported.

This hypothesis was questioned several years later by L. D. Hammond, who, in the article previously mentioned, concluded "from theoretical considerations the hypothesis that a film of electrolyte alkaline in reaction next to the cathode, is a condition necessary to secure a good deposit, is untenable and, practically, it is well known that the electrolyte must be slightly acid in reaction to secure the same result."

In the light of our present knowledge, it would seem that the matter simply resolves itself into one of definition. If we substitute the expression "film of minimum acidity" for "alkaline film" (since it is assumed that Bennett and his associates did not use high enough concentrations of ammonia to form a strictly ammoniacal solution), the views of Bennett and Hammond become completely harmonized. In a private communication, Hammond states his agreement with this conclusion drawn by the present writer.

That the film at the cathode may be less acid than the body of the solution, has been shown by unpublished experiments made at this Bureau by H. E. Haring. He conducted an electrolysis in a still nickel solution, and removed the cathode quickly at intervals and drained it. The pH of the sample of solution thus obtained was found to be appreciably higher than that of the body of the solution. If, then, it is the pH of the cathode film that determines the character of the deposit, this is the property which should be measured. No satisfactory method has been suggested, however, for determining the pH of this film with any degree of accuracy. In the absence of such data, measurements of pH on the body of the solution may be interpreted, upon the assumption that for a given solution and conditions of operation there is a definite relation between such values and those in the cathode film.

The probable and permissible difference in pH between the body and the cathode film of solution will depend upon its buffer characteristics. In a well buffered solution, such as the fluoride, the body of the solution must be more nearly neutral (higher pH) than in the chloride solution, in order to permit a cathode film of any desired pH (for the sake of illustration, 6.5) to be formed. Hence we find that, although it is much easier to maintain the pH of a fluoride than of a chloride solution within certain limits, this advantage is in part counteracted by the fact that in the fluoride solution the pH must be kept within narrower limits to yield equally high efficiencies. The decrease in efficiency produced by agitating the solutions, attributed by Bennett to the destruction of the "alkaline film," is likely to be least marked in solutions having an initially high pH.

The data on cathode efficiency may then be summarized as follows:

1. The cathode efficiency is increased either by raising the current density or the pH, or both.

2. Near pH 6, or above, the current density has little effect upon the current efficiency.

3. If it is desired, for any special reason, to operate a bath at a comparatively low pH (high acidity), raising the current density will help to compensate for the loss in current efficiency. If, however, it is necessary to operate at a low current density, solutions of high pH must be employed to secure high efficiency.

(*b*) *Relation between pH and the appearance and properties of deposits* (*color, pitting, curling, structure, strength, etc.*).

This subject is naturally of the most immediate interest in commercial depositing, and definite conclusions are greatly to be desired. Although it is easy to control the pH of a nickel solution, to study the pH characteristics of different types of baths, and to determine the effect of pH on efficiency, it is not yet possible to make precise statements on the relation between pH and the appearance and structure of deposits.

A large number of deposits were made from nickel sulphate solutions, containing boric acid and chlorides or fluorides. The current densities ranged from 0.2 amp./dm.^{2} (1.9 amp./sq. ft.)

to 2.0 amp./dm.^{2} (18.6 amp./sq. ft.). Cast anodes of 95 to 97 percent nickel were used, covered with cotton bags. Some deposits were made upon steel and others upon polished brass. In most cases the deposits had an average thickness of 0.013 mm. (0.0005 inch), corresponding to 1 amp.-hr./dm.^{2} (9.3 amp-hr./sq. ft.).

The following tentative conclusions were drawn from these experiments:

1. Below pH 3 and up to 4, gas pits and streaks, which are usually attributed to hydrogen evolution, are very pronounced. Cracking and peeling of deposits are generally encountered in this range. The nickel is usually rather bright.

2. Between pH 4 and 5.5, gas pits and streaks may appear, but are not likely to be pronounced, and cracking or curling is less common. The nickel is likely to be less bright in color.

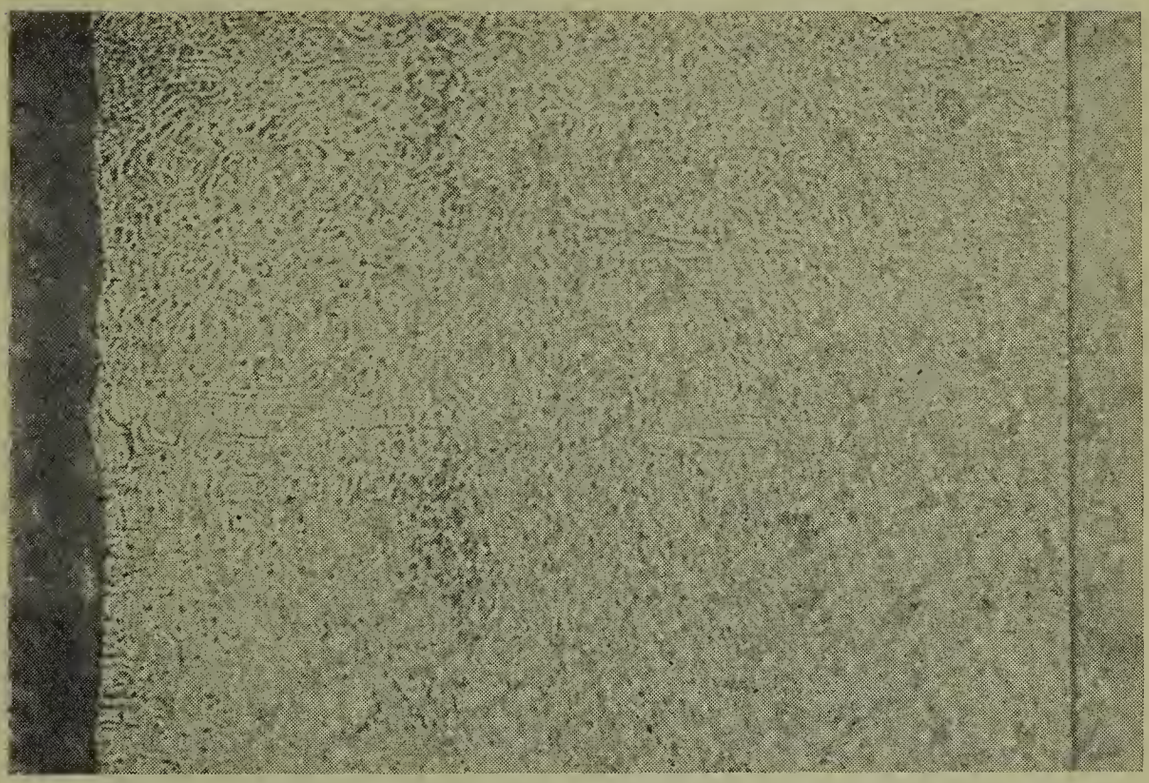
3. Between pH 5.5 and 6.5, gas pits and streaks are only rarely encountered. Above pH 6.3, blistering, cracking or curling are again likely to occur, also "burning" of the deposit near sharp edges, especially with high current densities. This is characterized by dark or black bands or patches. The nickel appears grayer in color, verging toward bluish near the upper limit of pH. Above pH 6.5 it seems difficult to get good deposits in still solutions. In agitated electrotyping solutions good deposits may be obtained up to nearly pH 7.0

The micro-structure of a few deposits in cross section is shown in Fig. 4. These deposits were made from solutions similar to those in Table IV, but with 0.25 *N* sodium chloride and fluoride, upon highly polished brass plates under the conditions previously described and at an average current density of 1 amp./dm.^{2} (9.3 amp./sq. ft.) for 20 hours. The micrographs were made from specimens cut from the central portions of the cathode plates. The thickness of deposit at these points is about 0.18 mm. (0.007 inch), between the brass cathode plate and a deposit of copper used to protect the surface of the specimen. The question arises as to whether these structures are comparable with those existing in the very thin commercial plating deposits, which are usually not over 1/10 or even 1/20 the thickness of these heavy deposits. The study of other metals shows that thick deposits exaggerate

(a) pH 3.30 x500

(b) pH 5.70 x500

FIG. 4. (a) and (b), deposits from chloride solution.



(c) pH 3.45 x500

(d) pH 5.85 x500

FIG. 4. (c) and (d), deposits from fluoride solution.

differences in the structure of thinner deposits. It seems certain, however, that any pronounced differences in the structure of thick deposits are indicative of similar if not equal differences in the structure of thin deposits or, at least, that any differences in structure will be in the same direction.

The pictures in Fig. 4 indicate that, in the chloride solutions, lowering the pH (increasing the acidity) tends to reduce the crystal size and *vice versa*. This is in accord with the well known fact that within certain limits excessive acidity tends to produce bright, hence fine grained, nickel deposits. Changing the pH of the fluoride solutions does not alter the crystal structure as much as in chloride solutions.

Those fluoride deposits which have a fine structure have been shown to possess great hardness and tensile strength.[12] In a private communication Geo. B. Hogaboom has called attention to the fact that in the paper by Wm. Blum, just referred to, no measurements of the pH were made upon the chloride and fluoride solutions used to prepare the specimens for the tensile strength tests, which were made before the pH method was applied to these solutions. Mr. Hogaboom made the very valuable suggestion that part at least of the differences in structure and properties of the two deposits may have been due to differences in the pH of the solutions.

The fact that, as shown in Fig. 4, much finer grained deposits were secured in the more acid than in the nearly neutral chloride solutions confirms this prediction, and emphasizes the importance of measuring the pH of solutions used in research. It is probable that deposits with greater hardness and tensile strength can be produced in chloride solutions that are more acid than those commonly used. It is difficult, however, to secure good deposits from relatively acid nickel solutions, and, therefore, the fluoride solutions, which give fine grained deposits at a high pH, have certain advantages when hardness is of importance.

VII. OBSERVATIONS ON THE pH OF COMMERCIAL PLATING SOLUTIONS.

In order to determine whether, in the actual nickel plating operation, the best results are secured within a definite range of

[12] Wm. Blum—The Use of Fluorides in Solutions for Nickel Deposition—Trans. Am. Electrochem. Soc., 1921, **39**, 227.

acidity, arrangements were made to obtain systematic observations on the pH of the nickel solutions in several large plants. This information was secured through the co-operation and courtesy of the Research Committee of the American Electroplaters' Society and the following persons: Wm. Delage, Jos. Haas, Jr., Geo. B. Hogaboom, H. M. Johnquest.

For a period of several weeks, pH tests by the Gillespie method, using methyl red, were made on the nickel solutions, which were controlled by the regular methods of analysis, without regard to pH. The results of over 100 pH measurements in these four plants showed that, when the solutions are satisfactorily operated, the pH is fairly constant. The extreme limits observed were pH 5.0 and 6.1, but most of the results were between 5.4 and 6.0, with an average in each plant of 5.7. These results were secured in solutions of the regular type, consisting usually of nickel sulphate, nickel ammonium sulphate, ammonium chloride and boric acid. A great variety of work is plated in these plants, in still tanks, plating barrels, and mechanical platers.

The only conclusion that can be drawn from these observations is that, under good commercial conditions, especially if maintained by chemical analysis, the solutions have a fairly constant pH, of 5.7 ± 0.3. If this is readily maintained by existing methods, there may be no advantage in using pH measurements for control work, unless thereby the time required for routine analytical work may be reduced. No definite evidence was secured regarding the effects of a pH outside of these limits, but the fact that long experience has led to the selection of operating conditions which maintain a nearly constant pH is significant.

The value of a simple, inexpensive test such as this will probably be greater for those plants in which facilities for detailed analytical control are not available. Even if, as is obvious, a knowledge and control of pH will not of itself insure satisfactory deposition, it will at least eliminate one of the variable factors in nickel plating. Arrangements were recently made to have the method applied in several plants operating without regular chemical analyses. Preliminary results indicate that some of these plants have operated with a pH between 5.8 and 6.2. This range is slightly different from that in the previous four plants,

and it remains to be seen whether in the latter equally good or better results may not be secured at a slightly lower pH. Further information will be published after the completion of these tests.

VIII. SUMMARY.

1. A simple method has been applied to the quantitative measurement and control of the pH (hydrogen ion concentration) of nickel depositing solutions by means of indicators.

2. The pH characteristics of several types of nickel plating solutions have been studied.

3. Preliminary observations have been made on the general effect of pH on the appearance and structure of nickel deposits.

4. The range of pH used in commercial nickel plating has been investigated.

5. A plea is made for the inclusion of complete pH data in all future publications dealing with research on the electrodeposition of such metals as nickel, cobalt and iron.

The writer desires to express his acknowledgments to Dr. Wm. Blum, under whose direction this work has been carried on; to Mr. J. H. Winkler, who prepared the electrolytic deposits; to Mr. Howard Scott, who prepared the micrographs; to his associates at the Bureau of Standards, who furnished criticisms and suggestions, and to the chemists and plating supervisors who supplied the data on commercial solutions.

DISCUSSION.

C. H. Proctor[1]: Mr. Thompson should be congratulated by the members of the American Electroplaters' Society who deposit nickel on their product because Mr. Thompson's paper takes the determination of acids in nickel solutions out of the rule-of-thumb field and gives it a more scientific aspect. Many platers have been accustomed to use the litmus and Congo paper determination, which, of course, we know does not give a scientific determination of the acidity of solutions, and I believe that it is a distinct step in

[1] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.

advance of the science of nickel plating, because in many instances the acidity has been too low or not high enough. The reason for this is the electroplater. If he uses very weak acids, such as boracic acid, it takes considerable time before he realizes the beneficial effects of such a weak acid. If he uses a strong acid, such as sulphuric acid, he is liable to overcharge his solution and the results are evolution of hydrogen rather than the deposition of nickel, and so by this new determination he will be able to produce more conclusive evidence of the action of acids upon the nickel solutions.

E. A. VUILLEUMIER[2]: There is a tendency to attribute the peeling of nickel deposits to the hydrogen that is known to alloy itself with the nickel deposited. The hydrogen content of the deposit may or may not be a function of the pH. It is possible, however, to show that the hydrogen, instead of favoring exfoliation tends rather to work in the opposite direction.

When nickel is deposited upon a thin platinum cathode, the cathode bends toward the anode. The degree of this contraction may be accurately measured by means of the "contractometer", as described in the Metal Industry, October, 1921, p. 419 and March, 1922, p. 109. There is reason to believe that this spontaneous tendency to contract is one of the important factors in peeling. If, however, hydrogen is liberated on the nickeled cathode, the bending is actually in the opposite direction.

G. B. HOGABOOM[3]: In the results given of the work done with the contractometer, no reference is made of the effect of the uneven distribution of the deposit, an effect that is well known in electrodeposition. When a sheet of metal, such as used in the contractometer experiments, is electroplated with nickel, it will be found that the bottom and the area nearly at the top receives a much heavier deposit than the center. It would be interesting to know whether such a condition would not tend to "buckle" the cathode and cause the needle of the contractometer to deflect. "Buckling" or the curving of the deposit is often experienced in heavy electrotypes.

E. A. VUILLEUMIER: The experiments I have been performing limited themselves to deposits that were very thin, and you could

[2] Professor of Chemistry, Dickinson College, Carlisle, Pa.
[3] Research Electroplater, Scovill Mfg. Co., Waterbury, Conn.

not notice any such phenomenon as this. Does this refer to nickel deposits a sixteenth of an inch thick or even thinner?

G. B. HOGABOOM: The deposits referred to would average about 0.004 inch in the thickest part. Just what the thinnest part measured is not known.

E. A. VUILLEUMIER: I do not know that I can answer Mr. Hogaboom's question. The results that we got were reproducible and I think are of interest, even in view of the experiments which he has discussed. If you deposit nickel on a thin sheet of platinum, the pointer bends and it moves quite uniformly. I do not see any connection between our results and these observations.

WM. BLUM[4]: If there were a tendency to bend might it not be accentuated by any irregular distribution of metal?

E. A. VUILLEUMIER: Thank you. I believe Dr. Blum has answered Mr. Hogaboom's question.

A. K. GRAHAM[5]: You will all agree with me, I think, that in making a deposit of nickel on a cathode of soft sheet zinc the cathode is decidedly embrittled just by a thin deposit of nickel. By simply flashing the cathode with a very thin deposit of nickel and then by cutting down the time, one can limit the deposits to a thin rim of metal around the edges, showing that this tendency mentioned by Mr. Hogaboom is in existance from the very beginning. Whether the bending effect is due to the same cause that the embrittling can be attributed to, I do not know. It seems likely, however, that it is this uneven deposit at the edges and the resulting tension which is greater where the deposit is thickest which probably accounts for this bending.

A. L. FEILD[6]: It is difficult for me to see how a small "hump" on a strip of platinum can bend the latter into what appears to be the arc of a circle. However, we know that electrodeposited metals come out of solution with very high internal stresses. In a number of cases these stresses have been measured in terms of pounds per square inch by determining the thickness of the deposit and the radius and length of the arc through which the electrode is bent. In the case of electrodeposited iron, this internal stress

[4] Chemist, Bureau of Standards, Washington, D. C.
[5] Chem. Eng., Philadelphia, Pa.
[6] Carbide and Carbon Res. Lab., Long Island City, N. Y.

amounts to something like 20,000 lb. per sq. in., a figure above the yield point of the same iron after vacuum-fusion and annealing.

C. P. MADSEN[7]: Dr. Thompson's effort to provide a simple means for determining the acidity of nickel depositing baths is commendable. I question, however, the correctness of assigning pH values to the determinations made with any indicator upon strong electrolytes, particularly if such determinations are made upon the electrolytes in dilute form. Clark[8] questions the application of the whole hydrogen ion theory developed for dilute electrolytes to that of very strong electrolytes, and points out that the millivolt reading taken on such solutions may mean many other things than that of hydrogen ion concentration.

I feel, furthermore, that the importance of the acidity of a nickel solution is over-estimated. I have found that other factors are far more important than the degree of acidity, and a condition can be established in the electro-deposition of nickel in which the degree of acidity plays but little part. If the anodes of proper composition are used, not only is the influence of the degree of acidity minimized, but is automatically corrected. It would therefore be very wrong to give practical operators the impression that the use of any indicator will cure his troubles. Furthermore, the meaning of color indications may pertain only to one particular type of solution and condition, and may not necessarily apply universally to all solutions and conditions. They can, however, be useful when standardized with relation to practical results in any given solution when operated with anodes of the same composition, but that is all.

WM. BLUM: In all the nickel plating solutions, there are hydrogen ions and they have an effect on the deposit; therefore, it seems desirable to measure them as accurately as we can in order to determine how much of the effect is due to them and how much is due to other factors or other impurities in the solution. That, I think, summarizes the discussion.

M. R. THOMPSON: Mr. Hogaboom has emphasized that the pH test is simply an adjunct to the analytical control of solutions. We still need to know the analysis. Unless a "titration

[7] Consulting Engr., New York City.

[8] "Determinations of Hydrogen Ions," Chapter 15, by W. Mansfield Clark. Williams & Wilkins Co., Baltimore, 1920.

curve" is at hand for a given solution, it is quite true that the pH value does not afford a means of calculating the quantity of acid or alkali necessary to add to maintain the solution at a fixed point. The titration method, using sodium alizarinsulphonate to indicate the end point, does give such information. We have attempted to bring these points out in the paper. There are prospects that a titration method, using brom cresol purple to indicate the end point, will be the best method yet developed for the commercial control of solutions. There is the great advantage, with the latter indicator, that the neutral point seems to be almost identical with the pH usually found in practice when solutions are giving satisfactory deposits. Obviously, any acidity or alkalinity found by this titration should be neutralized by an equivalent addition to the plating bath. Furthermore, results on different baths are more strictly comparable. The pH value, however, will always be an important constant to know.

Dr. Vuilleumier has discussed the effect of hydrogen evolution on nickel deposits and the application of the contractometer to measure the tendency of a deposit to curl. We would call attention to the fact that, in commercial plating, the pH is kept high enough and the current density at a point such that there is seldom any visible evolution of hydrogen. The current efficiency (in metal) is generally very close to 100 percent.

Mr. Madsen states that eight hours may be required for a reading to become constant, when using the hydrogen electrode apparatus. Only a few minutes are required to get a similar result by the use of an indicator. Perhaps, with our strong solutions, we do not know exactly what we have got in either case, but we call it the hydrogen ion concentration and make as good use of the result in the one case as in the other. The indicator method unquestionably has the advantages of simplicity and speed.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

A STUDY OF THE THROWING POWER AND CURRENT EFFICIENCY OF ZINC PLATING SOLUTIONS.[1]

By W. Grenville Horsch[2] and Tyler Fuwa[2]

Abstract.

This paper gives the results of a comparison of four distinct types of zinc plating solution. The effect of modifications in the composition of each type was studied. Using a three-section cathode, the throwing power, cathodic current efficiency, and cell voltage were determined for each bath and modifications. An alkaline cyanide bath was found to give the greatest throwing power; and by the device of employing an insoluble anode in parallel with the zinc anode of such area as to carry about 20 percent of the current, such a bath could be made to give constant results for weeks by simply replenishing from time to time with small amounts of addition agent.

INTRODUCTION.

The object of this study[3] was the development of a zinc plating bath of high "throwing power," that is, a bath which would permit a uniform distribution of the deposit even on objects of irregular contour, and one which at the same time would yield firmly adherent and reasonably smooth deposits. The attainment of the highest possible degree of luster and otherwise good appearance was considered of secondary importance.

In order to make clear the reasons for trying certain solutions, and in order to explain the results obtained, it seems desirable to

[1] Manuscript received March 14, 1922.

[2] Contribution from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology.

[3] The investigation was financed by the National Tube Co., and is published with their kind permission. Thanks are due to Mr. F. N. Speller, metallurgical engineer, of that Company, for suggesting the investigation. The authors also take the opportunity to acknowledge the many helpful suggestions of Professor R. E. Wilson, Director of the Laboratory, and the assistance of Mr. D. H. Cameron in part of the experimental work.

discuss the general theory of throwing power which guided this work. In order that a plating bath may possess high throwing power, it is necessary to have present in solution a large total number of conducting ions, but a relatively small number of free ions of the metal plated out. This may be explained as follows: Consider a cathode placed at right angles to an anode so that one part of the cathode is much nearer than the other to the anode. The relative amounts of current which will go to the near and to the distant points of the cathode will depend upon the relative resistances of the two paths. The resistance of these paths may be divided into two portions—one, that through the solution proper; and the other, that through a film on the surface of the cathode. The latter resistance is considered to include overvoltage and polarization effects.

The first of these two resistances obviously is greater for the long path, than for the short path. It is assumed, as seems reasonable, that the current efficiency at each unit area of the cathode is the same. Therefore, the way to make the current density approach equality on each unit area of the cathode, and consequently obtain a uniform distribution of the deposit, is to make the first (or solution) resistance as low as possible, and the second (or film) resistance high. Then the difference between the total resistance of the two paths will tend to be eliminated because the "film" resistance, since it includes polarization, will be greatest at that point on the cathode where the current density is greatest, whereas the resistance through the solution is proportional to the length of path.

As already stated, by having a small number of free ions present in the solution, polarization takes place very readily. This effect can be accomplished most easily by the use of salts which are either slightly ionized, or which form complex ions of the metal. These ideas are confirmed by the experimental results, to be described presently, obtained with cyanide baths of high free alkali content.

There is, of course, no novelty in the use of cyanide baths to secure high throwing power. Very little work has been published, however, which gives a quantitative idea of the way this factor varies under different conditions and with various baths.

Alkaline cyanide baths have been recommended for furnishing a rust-proof preliminary coating on auto lamp reflectors[4] and for irregular objects[5] in general. They have also been used in finish process galvanizing of steel stampings;[6] for "strike" solutions in galvanizing booster cases;[7] and in European work.[8] The Bureau of Standards[9] also recommends a certain bath containing cyanide. There is a wide variation in the composition of these various baths, both with respect to the cyanide content and the quantity and nature of other materials present.

Wernlund[10] in a recent paper has taken a good step toward the establishment of the zinc cyanide plating solution on a sound scientific basis. He determined the chemical solubility of zinc in various electrolytes; studied deposits and anode corrosion with various solutions; compared fifteen addition agents; and determined the anodic and cathodic current efficiencies with various cyanide baths. He showed by plating automobile tire rims that the cyanide bath gave much more uniform deposits than the sulphate bath, as indicated by the Cushman test.[11] He found also that high sodium hydroxide content in cyanide baths was detrimental, causing fouling of the anode.

A bibliography of the general subject of zinc plating is given at the end of the present paper.

APPARATUS AND PROCEDURE.

The apparatus used in making the experimental runs with the various plating solutions is shown diagrammatically in Fig. 1 (a) The plating solution was put into a large hard rubber battery container fitted with a motor-driven stirrer; a small, glass steam coil served as a heater. The volume of solution used was about four liters; this varied not more than 5 percent with the different solutions.

[4] Proctor, Chas. H., Metal Industry, 1917, **15**, 149.

[5] Metal Industry 1920, **18**, 478.

[6] Pleadwell, W. B., Metal Industry, 1921, **19**, 323.

[7] Eidstaedt, T. C., Metal Industry, 1919, **17**, 22.

[8] Barclay, Metal Industry, 1921, **19**, 159.

[9] Blum, Wm., Liscomb, T. J., and Carson, C. M., Bureau of Standards, Tech. Paper 195, Oct. 17, 1921; Monthly Rev. Am. Electroplaters' Soc. Nov., Dec., '18 and Apr. '19; Brass World, 1919, **15**, 6.

[10] Wernlund, C. J., Trans. Am. Electrochem. Soc., 1921, **40**, 257.

[11] Cushman Test—U. S. Pat. 1,372,405. The weight of metallic coatings on iron and steel structures is determined by measuring the volume of evolved gas when hydrochloric acid is applied to a definite integral portion of the coated surface.

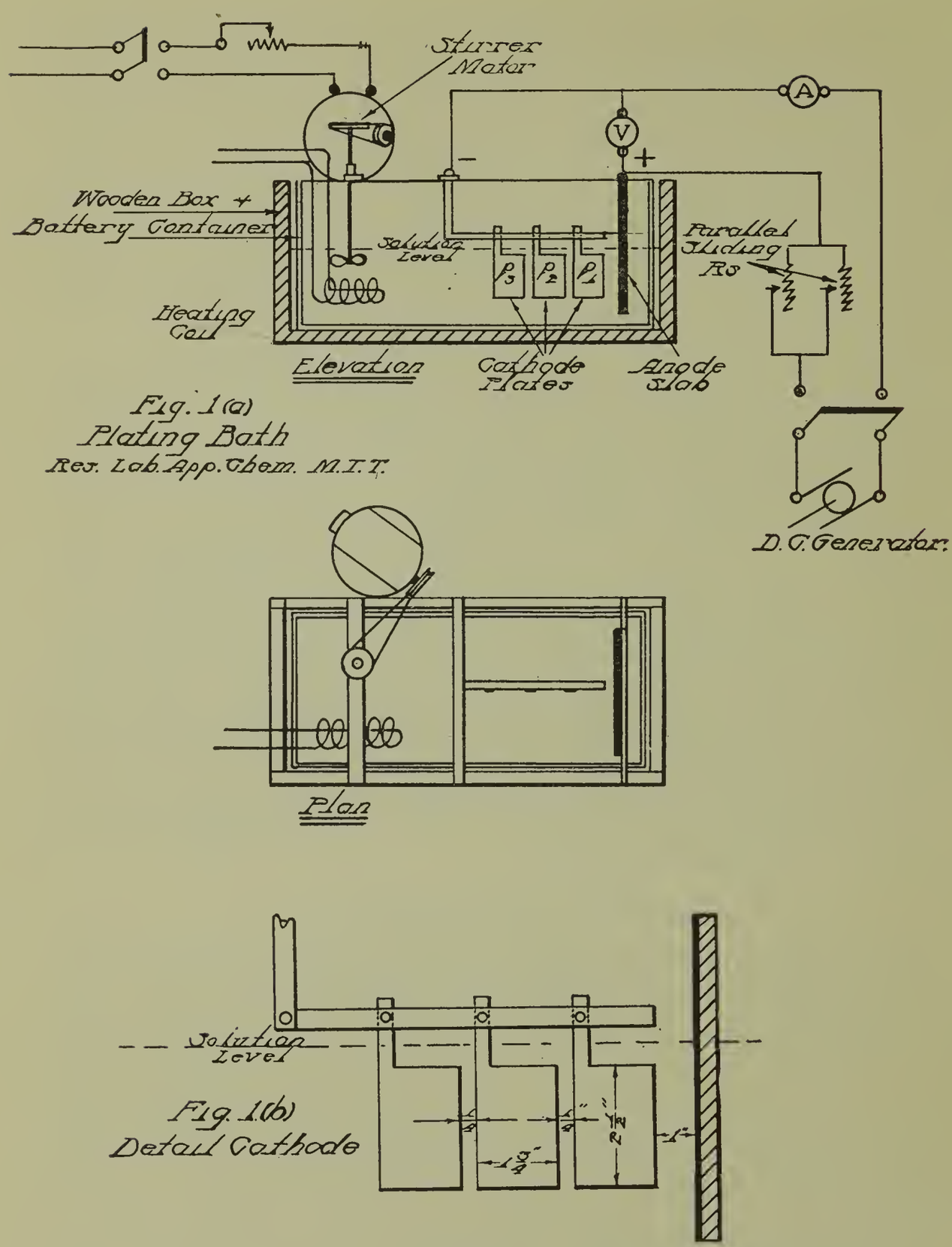


FIG. 1

A thick plate of commercial rolled or cast zinc served as the anode, and the cathode was made up of three identically shaped sheet iron plates, about 20 gauge, as shown in Fig. 1 (b). These cathode plates were so fastened to a bus bar that they could be detached and weighed readily before and after each run, thus

giving a quantitative measure of the throwing power and current efficiency. It will be noted that when attached, the cathode plates are aligned in a plane at right angles to the plane of the anode slab, the nearest plate being one inch from it, the two remaining plates being separated by one-quarter inch spaces.

Suitable sliding resistances were introduced into the stirrer and plating solution circuits, as well as the necessary meters. The loss by evaporation was kept at a minimum by a covering of plate glass over the bath.

The procedure used in making a typical run was as follows: The test plates were pickled in concentrated hydrochloric acid, washed in water, dried, weighed and then attached to the bus bar. The routine data recorded were current, voltage, solution temperature and degree of stirring. The latter was designated roughly as being moderate or rapid.

The occurrence of any unusual amount of gassing or other phenomena was also noted. A standard time of 10 minutes was usually taken as the duration of a run; however, many of the runs were for different periods, and several long runs were made. After plating the plates were quickly removed from the solution, washed, dried, weighed, and the character of the deposit noted.

From the recorded data, simple calculations give (1) the current efficiency of the three cathode plates as a whole, and (2) the throwing power, expressed in terms of the percentage of the total theoretical weight of zinc deposited on the three plates, which was deposited upon each of the three plates at varying distances from the anode. Special care was taken thoroughly to clean the plates and also the anode surface before each measured run.

EXPERIMENTAL RESULTS.

The experimental work described in this paper consisted, first, in a preliminary study, in which the properties of seven different plating solutions were compared; and, second, in an intensive study of alkaline zinc cyanide baths, after it had been shown that the latter gave by far the highest throwing power.

The compositions of the various baths are given below, and the results with each discussed. It will be noted that the concentration in each case is expressed in grams of each constituent per

liter of water. Slight modifications in, or additions to them, were sometimes made in the course of the experiments. Such modifications were noted, and the numerical data are recorded in Table I, which gives for each run the cathodic current density, cell voltage, temperature, amount of stirring, average cathodic current efficiency and the throwing power as indicated by the percent of the total theoretical amount of zinc deposited which was deposited on each of the three cathode plates.

A summary of the experimental data is also given in graphic form in Fig. 2, to be referred to more fully later.

A. Preliminary Study of Various Baths.

A commercial plating solution of the following composition was first studied:

Solution No. 1—Zinc Sulphate

Zinc Sulphate	277.5	grams
Aluminum Sulphate	7.7	"
Water	1000	cc.

It will be noted from Table I that the outstanding characteristics of this solution are (1) high current efficiency, (2) poor throwing power (very unequal distribution over the three plates), and (3) a tendency to form crystalline aggregates, especially on the edge nearest the anode. There is no marked evidence that results are improved by an increase in the rate of stirring, or by considerable elevation in temperature. Increasing the current density while keeping the other factors constant tends to improve the throwing power slightly.

According to the literature, zinc cyanide solutions have had wide industrial use; one of the successful formulas[12] being equivalent to the following:

Solution No. 2—Cyanide "A"

Sodium Cyanide	106.0	grams
Sodium Carbonate	8.2	"
Aluminum Sulphate	3.5	"
Zinc Oxide	43.1	"
Sodium Hydroxide	2.3	"
Licorice Powder	0.5	"
Water	1000	cc.

[12] Metal Industry, 1920, 18, 478.

The results of runs made with this solution are given in Table I. This group of runs is characterized by (1) a comparatively low current efficiency, (2) much better throwing power than is shown by solution No. 1, (3) smooth and uniform character of deposits, and (4) uniformity of results over a considerable range of current densities.

It was found experimentally that in 225 gm. of water, 28.75 gm. of zinc cyanide would dissolve in the presence of 25 gm. of sodium cyanide and 1 gm. of sodium hydroxide at 25° C. Using this as a basis, another cyanide solution was made up in an attempt to simplify solution No. 2:

Solution No. 3—Cyanide "B"

Zinc Cyanide	128.0	grams
Sodium Cyanide	110.6	"
Sodium Hydroxide	5.0	"
Water	1000	cc.

In general, the characteristics of this solution were the same as those of solution No. 2. There was a marked tendency towards anode polarization, however, and considerable gassing on cathode plate 1. As indicated by Table I (third section), successive additions of 74.5 gm. sodium sulphate did not affect the results materially. By using a fresh solution to which 12.4 gm. of sodium cyanide had been added, anodic polarization was prevented, and the throwing power increased; the current efficiency still remained poor.

Starting again with a fresh solution, 12.4 gm. of sodium hydroxide was added. This increase in alkalinity caused a marked improvement in the current efficiency; however, the deposits were granular and badly stained.

The possibility of using a sodium zincate solution for plating was next investigated. Sodium zincate may be formed according to the equation—

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

Although the stoichiometrical amounts of zinc oxide and sodium hydroxide are as 81.4 to 80.0, the maximum allowable con-

TABLE I.

Results of 10-Minute Runs with Various Baths.

Run No.	Current Density Amp./Dm²	Avg. Voltage	Temp. Solution °C	Rate of Stirring	Throwing Power: percent of Total Theoretical Zinc on Plate 1	Plate 2	Plate 3	Cathodic Current Efficiency	Composition of Bath Gm. per liter H_2O						See Page 372
Solution No. 1,—Sulphate									$ZnSO_4$	$Al_2(SO_4)_3$					
2	1.08	2.0	25	Still.....	68.2	16.6	12.4	97.2	277.5	7.7	...	..	..	..	(1)
3	2.15	3.8	25	Still.....	63.6	16.0	16.1	95.7	277.5	7.7	...	..	..	..	(1)
4	3.23	4.5	25	Still.....	51.8	13.0	14.5	79.3	277.5	7.7	...	..	..	..	(2)
5	3.23	4.6	25	Moderate..	56.9	17.4	21.2	95.5	277.5	7.7	...	..	..		
6	2.15	4.3	25	Moderate..	73.9	15.3	8.7	97.9	277.5	7.7	...	..	..	..	(3)
10	2.15	2.3	66	Rapid.....	74.6	15.5	8.5	98.6	277.5	7.7	...	..	..	..	(4)
Solution No. 2,—Cyanide "A"									NaCn	Na_2CO_3	$Al_2(SO_4)_3$	ZnO	NaOH	Licorice	
12	2.15	2.0	35	Rapid.....	22.7	17.3	12.7	52.7	106.0	8.2	3.5	43.1	2.3	0.5	(5)
13	3.23	2.8	32	Rapid.....	16.4	12.4	10.7	39.5	106.0	8.2	3.5	43.1	2.3	0.5	(5)
14	4.30	4.5	28	Rapid.....	15.6	9.6	9.8	35.0	106.0	8.2	3.5	43.1	2.3	0.5	(6)
Solution No. 3,—Cyanide "B"									$Zn(CN)_2$	NaCN	NaOH	Na_2SO_4			
16	3.23	8.5	25	Slow.....	15.0	7.9	7.9	30.8	128.0	110.6	5.0	...	..	..	(7)
18	1.08	3.5	25	Slow.....	25.7	13.1	6.6	45.4	128.0	110.6	5.0	74.5	..	..	(8)
28	2.15	2.1	25	Moderate..	3.7	2.1	2.2	8.0	128.0	123.0	5.0	149.0	..	..	(9)
32	2.15	2.1	25	Moderate..	21.5	14.2	9.1	45	128.0	110.6	17.4	...	..	..	(10)
33	3.23	4.7	25	Moderate..	19.6	12.0	7.4	39	128.0	110.6	17.4	...	..	..	(10)
Solution No. 4,—Sodium Zincate									ZnO	NaOH	NaCN	Casein	Licorice		
37	2.15	0.8	25	Moderate.	53.9	18.3	9.0	81	32.1	363.0	...	...	..	..	(11)
40	2.15	0.9	25	Rapid.....	55.9	17.7	9.2	83	32.1	363.0	...	14.0	..	..	(12)
46	0.72	0.3	42	Rapid.....	53.8	17.6	9.7	82	32.1	363.0	...	14.0	..	..	(13)
48	2.15	0.9	40	Rapid.....	39.5	20.9	14.2	75	32.1	363.0	14.0	...	1.4	..	(14)

Solution No. 5,—Fluoborate "A"									H_2O	$ZnSO_4$	NaF	H_3BO_3	Glue		
49	2.15	5.0	22	Moderate..	74.0	15.3	7.6	98.1	1000	321.0	8.2	31.3	..	..	(15)
50	2.15	4.4	23	Moderate..	71.6	14.9	8.3	95.0	1000	321.0	8.2	31.3	13.6	..	(16)
51	2.15	4.3	23	VeryRapid	72.2	14.9	8.3	95.6	1250	321.0	8.2	31.3	13.6	..	(17)
Solution No. 6,—Zinc Fluoborate "B"									H_2O	HF (50%)	H_3BO_3	$ZnCO_3$	Glue		
56	3.23	3.3	25	VeryRapid	75.9	14.2	6.5	97.0	1000	303.8	141.9	79.3	..	..	(18)
63	2.15	2.5	25	VeryRapid	49.2	21.4	9.1	79.7	1000	303.8	141.9	79.3	7.6	..	(19)
64	3.23	4.9	25	VeryRapid	46.9	13.0	5.6	65.6	1750	303.8	141.9	79.3	15.2	..	(20)
65	3.23	2.8	61	VeryRapid	60.4	15.3	6.8	82.6	1750	303.8	141.9	79.3	22.8	..	(21)
Solution No. 7,—Zinc Ammonium Sulphate									H_2O	$ZnSO_4$ $7H_2O$		$(NH_4)_2$ SO_4	Glue		
67	3.23	4.1	20	VeryRapid	81.1	12.1	5.9	99.0	1000	130.6	...	57.0	..	..	(22)
69	3.23	3.0	54	VeryRapid	56.9	18.0	8.5	83.7	1000	130.6	...	57.0	3.0	..	(23)
70	3.23	4.3	42	VeryRapid	46.4	15.6	8.3	70.3	1600	130.6	...	57.0	3.0	..	(24)
Solution No. 8,—Cyanide "C"									NaCN	$Zn(CN)_2$	NaOH	Na_2CO_3	Al_2 $(SO_4)_3$	Glue	
75	3.23	10.1	35	Moderate..	9.3	7.0	7.0	23.3	51.3	57.2	19.4	9.1	4.6	5.7	(25)
76	3.23	4.1	40	Moderate..	15.3	15.1	8.7	39.1	51.3	57.2	42.2	9.1	4.6	5.7	(26)
79	3.23	11.6	25	Moderate..	9.1	7.7	5.0	21.8	39.9	57.2	19.4	9.1	4.6	..	(27)
80	3.23	6.5	27	Moderate..	7.5	6.1	4.6	18.2	51.3	57.2	19.4	9.1	4.6	..	(28)
81	3.23	3.5	33	Moderate..	13.3	12.6	12.7	38.6	51.3	57.2	42.2	9.1	4.6	..	(29)
82	3.23	2.7	36	Moderate..	12.6	11.3	6.5	30.4	51.3	57.2	42.2	9.1	4.6	5.7	(30)
88	3.23	2.5	40	Moderate..	17.8	15.7	14.4	47.9	51.3	57.2	42.2	9.1	4.6	13.7	(31)
91	2.15	1.5	38	Moderate..	38.5	13.7	10.4	62.6	51.3	57.2	19.4	9.1	4.6	(*)	(32)
96	2.15	1.7	37	Moderate..	28.7	21.6	12.8	63.1	51.3	57.2	42.2	9.1	4.6	(†)	(33)
Solution No. 9,—Cyanide "D"									NaCN	Zn $(CN)_2$	NaOH	Na_2CO_3	Al_2 $(SO_4)_3$	Lignol	
101	2.15	1.6	40	Moderate..	31.0	25.6	24.3	80.9	53.2	59.2	43.8	9.5	4.7	11.8	(34)
105	2.15	1.6	40	Moderate..	45.0	25.0	12.0	82.0	53.2	59.2	43.8	9.5	4.7	11.8	(35)

* Run 91—Add 11.04 gm. Lignol per liter to Composition of Bath.

† Run 96—Add 4.6 gm. Lignol per liter to Composition of Bath.

Table I—Concluded

REMARKS

(1) Heavy treeing on edge Plate 1.
(2) Large crystals, edge of plate nearest anode.
(3) Fresh solution; same characteristics as Run No. 4.
(4) Deposits dull; no improvement over cold solution.
(5) Smooth adherent deposit.
(6) Some treeing on edge Plate 1.
(7) Good deposit plate 1; poor on plates 2 and 3; polarization occurred.
(8) Stopped polarization.
(9) Current efficiency very poor.
(10) Fresh bath; deposits stained.
(11) Deposit poor and spongy.
(12) No improvement.
(13) Lowered current density; no sponge.
(14) Increased current density; deposit very spongy.
(15) Deposit hard, but in coarse crystals.
(16) Some improvement in deposit.
(17) Treeing reduced somewhat.
(18) Extensive treeing.
(19) Considerable improvement in deposit.
(20) Further improvement in deposit.
(21) Solution temperature raised; current efficiency improved.
(22) Considerable treeing and spongy deposit on Plate 1.
(23) Considerable improvement in deposits.
(24) Further improvement in appearance of deposit.
(25) Deposits good, but polarization severe at cathode.
(26) Deposits good and polarization greatly reduced.
(27) Deposits good, but polarization severe.
(28) Deposits good, but thin.
(29) Current efficiency increased; some sponge on plates 2 and 3.
(30) Deposits improved markedly.
(31) Deposits very satisfactory.
(32) Marked increase in current efficiency; deposits good.
(33) Deposits good.
(34) Deposit very good and current efficiency high.
(35) Same bath as Run 101 after 20 hours of operation; decrease in throwing power but deposits good; no decrease in C. E.

centration of zinc oxide according to Seidell[13] is as shown in Solution No. 4.

Solution No. 4—Sodium Zincate

Zinc Oxide	32.1	grams
Sodium Hydroxide	363.0	"
Water	1000	cc.

The results given in the fourth section of Table I will show that in all essential respects, the zincate solution is very different from cyanide solutions A and B. There is little tendency to polarize and evolve excessive quantities of gas, the current efficiency is high, the deposits are spongy instead of being smooth, and the throwing power is poor. The high and even conductivity of this solution is due mostly to the high alkali concentration.

The use by Blum[14] of fluoborate in nickel plating suggests its use in zinc plating. Substituting zinc sulphate for nickel sulphate, mol for mol, in Blum's formula, a solution was made up having the composition:

Solution No. 5—Zinc Fluoborate "A"

Zinc Sulphate	321.0	grams
Sodium Fluoride	8.2	"
Boric Acid	31.3	"
Water	1000	cc.

In all of the runs with this solution, pronounced feathery, adherent coatings were formed, there being no tendency to form a loose, non-adherent deposit. The cathodic current efficiency of this solution is very high (90 to 98 percent), but the throwing power is poor. The addition of 13.6 gm. glue improved the surface of the deposit, but failed to increase the throwing power.

In connection with an article on lead plating, Blum[15] gives another fluoborate plating formula, which seems to have desirable qualities. In the case of zinc, the reactions whereby the metallic fluoborate is formed are:

$$4HF + H_3BO_3 \rightarrow HBF_4 + 3H_2O \qquad (1)$$

$$2HBF_4 + ZnCO_3 \rightarrow Zn(BF_4)_2 + H_2CO_3 \qquad (2)$$

The above reactions go to a theoretical completion. Blum recommends that the total fluoboric acid content be 1.5 mols per

[13] Seidell—Solubilities of Inorganic Compounds.
[14] Blum, William—Chem. and Met. Eng. 1921, 24, 1109.
[15] Blum, Wm.—Trans. Am. Electrochem. Soc. 1919, 36, 243.

liter, and that only two-thirds of this acidity be neutralized with carbonate, in this case zinc carbonate. There should be an excess of 20 percent free boric acid also. The composition of the following formula is consistent with Blum's recommendations:

Solution No. 6—Zinc Fluoborate "B"

Hydrofluoric Acid (50 percent)	303.8	grams
Boric Acid	141.9	"
Zinc Carbonate	56.6	"
Water	1000	cc.

As it was found that the zinc anode was dissolved rapidly by such a high acid concentration, 22.7 gm. zinc carbonate was added to correct this fault, making the total 79.3 gm. A few runs showed that this solution possessed the same characteristics as solution No. 5, epecially with respect to throwing power and appearance of the deposit.

In an attempt to modify these defects, 7.6 gm. glue was added. The only improvement was in the appearance of the deposit. Dilution of the solution with 750 cc. water, and a subsequent elevation of the solution temperature to 61° C. also failed to effect any substantial improvement in throwing power. The data on this solution are given in the sixth section of Table I, concluding the study of zinc fluoborate solutions.

Since the use of double ammonium salts has been recommended for certain plating solutions, an electrolyte was made up containing simply the double salt ammonium zinc sulphate, $(NH_4)_2Zn(SO_4)_2 . 6H_2O$. The solubility of the anhydrous salt at 20° C. is 12.6 gm. in 100 gm. water. The concentration was therefore made such that saturation would occur at 20°C.

Solution No. 7—Zinc Ammonium Sulphate

Zinc Sulphate (hydrated)	130.6	grams
Ammonium Sulphate	57.0	"
Water	1000	cc.

It will be noted that the several runs with this solution show a marked tendency toward spongy deposits, with high current efficiency and poor distribution, both at low and at elevated temperatures. The addition of 3 gm. of glue reduced the amount of sponginess, and with a further addition of 600 cc. water, the deposits became quite satisfactory; this, however, was at the expense of a much lowered current efficiency.

B. Intensive Study of Zinc Cyanide Solutions.

As a result of the work with various plating solutions, it was decided that cyanide solutions most nearly fulfilled the requirements of a successful plating bath. Below are given the results of experiments under a variety of conditions which led to the development of a bath which showed high throwing-power, satisfactory efficiency, and a high degree of permanence when operated under the conditions specified.

The basic formula to which all variations are referred is as follows:

Solution No. 8—Cyanide "C"

Sodium Cyanide	51.3	grams
Zinc Cyanide	57.2	"
Sodium Hydroxide	19.4	"
Sodium Carbonate	9.1	"
Aluminum Sulphate	4.6	"
Water	1000	cc.

This solution, used directly without modification, gave spongy deposits. The addition of 5.7 gm. glue suppressed this sponginess entirely, but there was severe polarization at the cathode. (Run 75, Table I). This polarization was found to be still greater with larger glue content. Run 76 shows how it was possible to reduce the polarization with glue present by adding 22.8 gm. NaOH.

High voltage and low efficiency were obtained with a fresh solution which contained about 11 gm. less NaCN than corresponds to the composition of solution 8. When the 11 gm. NaCN was subsequently added (making the total 51.3 gm.) polarization was reduced, but the efficiency and distribution were unchanged. (Run 80). The addition next of 22.8 gm. NaOH and a total of 13.7 gm. glue (Run 88) brought about a marked improvement with respect to all factors; and the character of the deposit was very satisfactory.

A fresh solution was made up, leaving out the aluminum sulphate and sodium carbonate, but the results were poor; the addition of 11 gm. lignol,[16] however, brought about a marked improvement (Run 91). A further addition of the amounts of aluminum sulphate and sodium carbonate required by formula 8

[16] A product of the Eastern Mfg. Co., Bangor, Maine; probably a sulfite liquor concentrate.

resulted in good deposits, showing that these salts have an important function in the plating solution.

In run 96—a fresh solution, to which 22.8 gm. NaOH had been added—the deposits were very uniform in nature, even with only

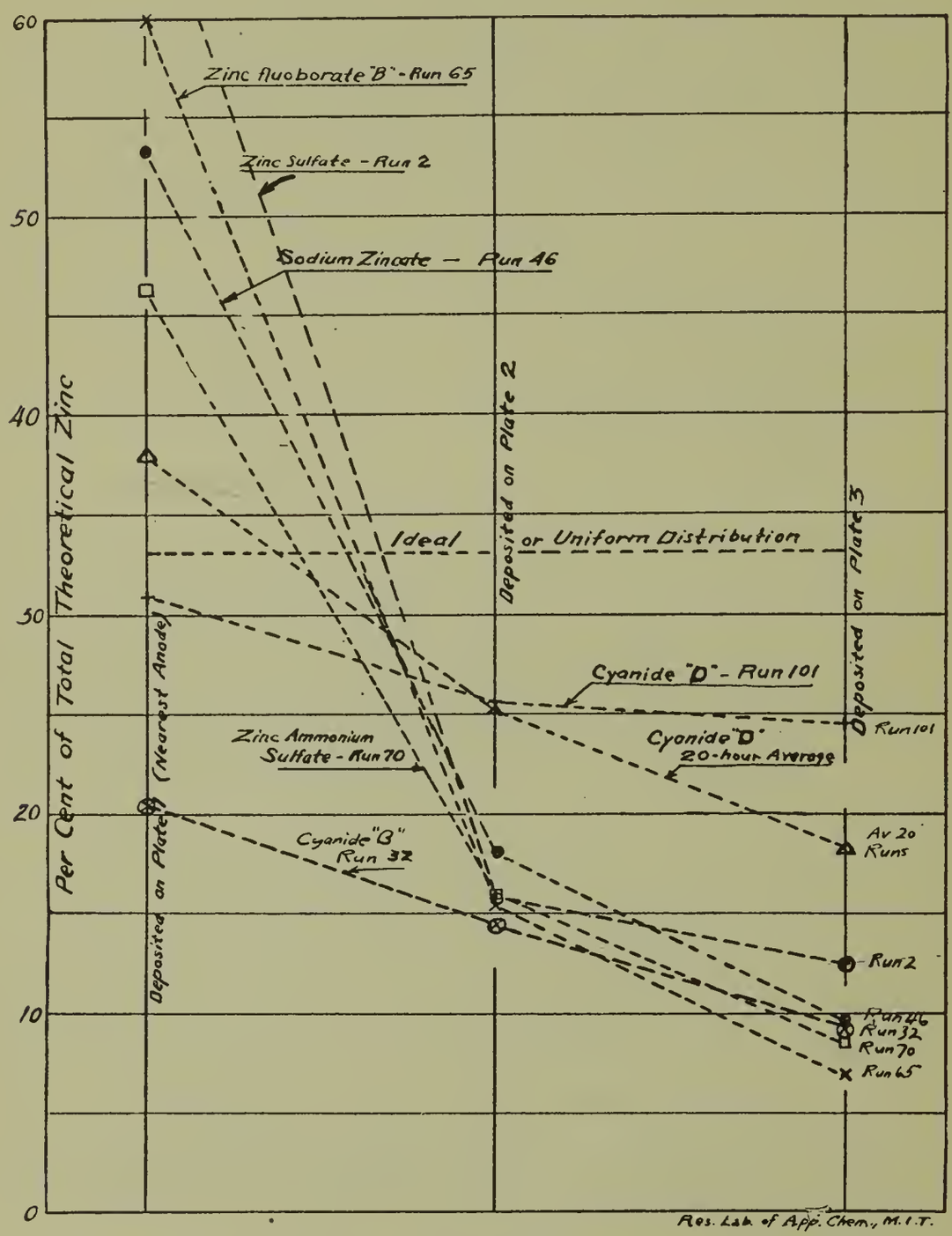


Fig. 2

4.6 gm. of lignol. Two check runs confirmed the behavior of this solution composition.

Now that a cyanide solution had been developed, which seemed satisfactory in every respect except, perhaps, as regards current efficiency, it seemed desirable to study the performance during

long continued operation, noting especially any attendant changes in the composition of the solution. Accordingly, a run of 20 hours was next made (see Runs 101 and 105) in which the above conditions were observed. The following solution composition was used for this run:

Solution No. 9—Cyanide "D"

Sodium Cyanide	53.2	grams
Zinc Cyanide	59.2	"
Sodium Hydroxide	43.8	"
Sodium Carbonate	9.5	"
Aluminum Sulphate	4.7	"
Lignol	11.8	"
Water	1000	cc.

The results of this run showed that although the nature of the deposit and the current efficiency could be kept fairly uniform, the throwing power fell off progressively.

Data obtained with this bath are presented graphically, and a comparison with the other types of bath studied are given in Fig. 2, wherein the percent of the total theoretical weight of zinc on the three plates (*i. e.,* that corresponding to the quantity of electricity passed) which was deposited on each of the three cathode plates is given. One set of results from each bath is given in the case of Cyanide "D," these results corresponding to the conditions which gave deposits of satisfactory character. In the case of Cyanide "D," two curves are plotted, the first being for run 101 which gave the best deposits, and the second being the average results over a 20-hour period, during which no additions were made to the bath. It will be noted that with the manner of plotting used, the curve for 100 percent efficiency and ideal or uniform distribution is a horizontal line passing through 33.3 percent. In the case of each curve, the sum of the ordinates of the three plotted points is equal to the overall cathodic current efficiency. The superiority of the results with Cyanide "D" over those with the other types of bath is evident.

The decline in throwing power with age of the cyanide bath may be attributed to at least two causes; (1) a progressive increase in the zinc content of the solution, and (2) a depletion of the addition agent with continued operation.

Since the current efficiency at which the zinc dissolves from the anode is substantially 100 percent, while the efficiency of

deposition on the cathode is only about 80 percent, there is a progressive increase in the zinc content of the solution. Furthermore, the 20 percent of current which does not deposit zinc at the anode, does evolve a corresponding amount of hydrogen gas and produce hydroxyl ions in solution at the cathode.

This increase in zinc content of the solution would soon go so far as to produce too many free zinc ions in solution, and thus impair the throwing power very seriously, if the suggested theory of throwing power is correct.

To correct this tendency, the current practice seems to consist of periodic additions of sodium cyanide, but it is obvious that such a procedure affords only a temperary relief, and also changes the solution composition markedly. One corrective measure worked out in this laboratory involves the use of oxalic acid, which has been found to restore the solution to normal by neutralizing the excess alkalinity, and simultaneously precipitating the desired amount of zinc. This procedure is costly, however, and introduces a precipitate in the bath.

The desired result may be accomplished by reducing the anodic current efficiency, by having part of the anode composed of practically insoluble material such as duriron. If 20 percent of the current is to go to this insoluble anode, it prevents the excess zinc from going into solution, and also forms acid at the anode, neutralizing the alkali formed simultaneously at the cathode. The solution is thus brought back substantially to its original composition. The relative area of insoluble anode required depends somewhat upon other conditions, but in general, if 30 percent of the anode area (meaning total including zinc) is duriron, the latter will carry about 20 percent of the current. In practice, it would be desirable to have variable external resistance, in series with the duriron, to permit adjustment of relative currents through the iron and zinc components.

A precise regulation of the relative currents through the two component parts of the anode is unnecessary, however, since there is a reasonable range of zinc concentrations, within which the bath behaves satisfactorily. Furthermore, a bath has a certain degree of inherent stability, in that if the zinc content gets too high, the current efficiency of cathodic deposition increases, and

hence the zinc content builds up less rapidly, if at all, and *vice versa* if the zinc content falls too low.

The anode plates, especially those of duriron, should be kept well below the surface of the solution; this will prevent the discharge of any HCN that might be evolved at the anode into the air of the cell room.

A continuous run of 180 hours, made by using a duriron and a zinc anode alternately, amply demonstrated that not only the

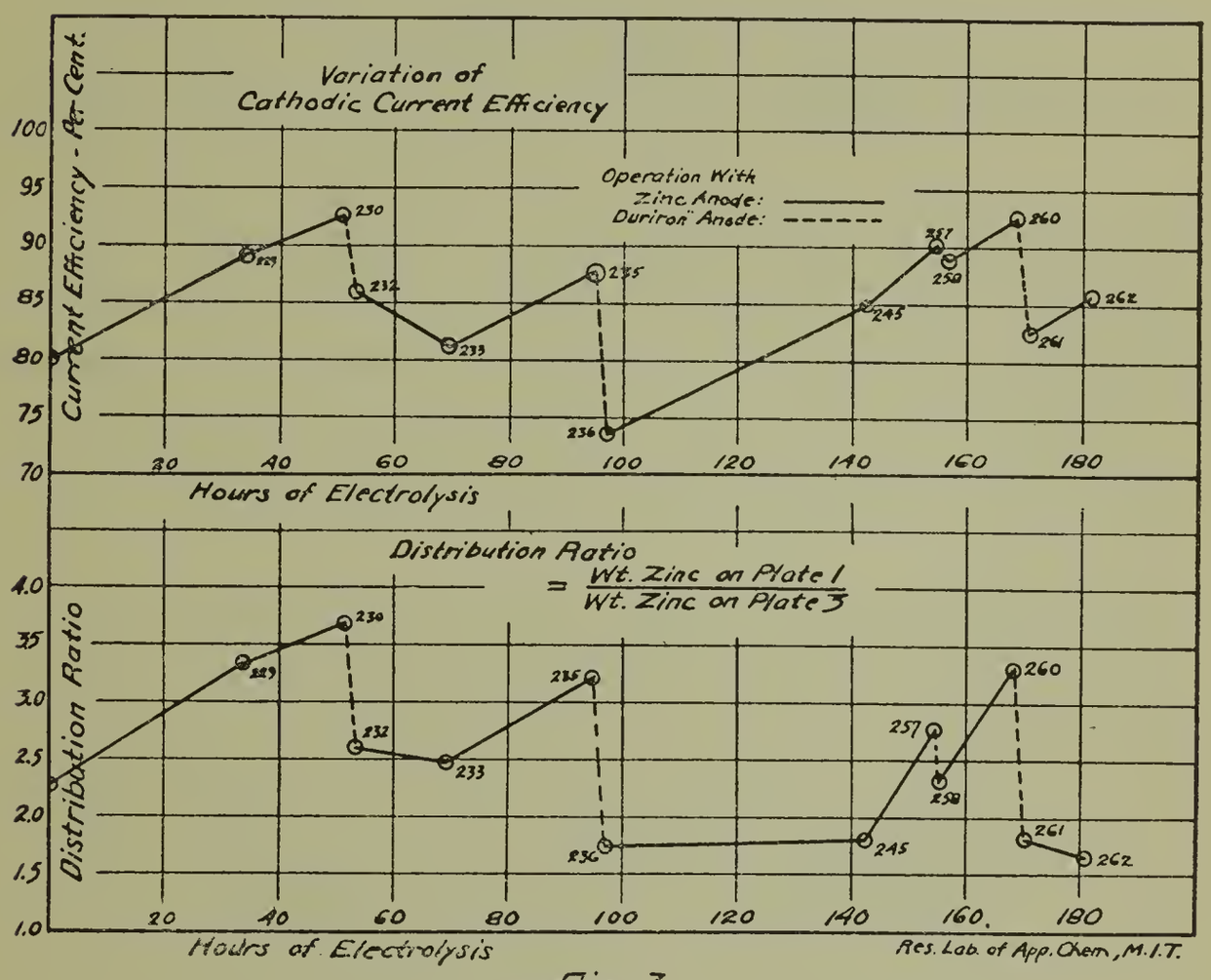


Fig. 3

throwing power, but other characteristics of the solution can be kept uniform over a long running period by means of this comparatively simple procedure. The cathodic current efficiency for the entire time averaged 80 percent, and no difficulties were experiened in obtaining good deposits. Figure 3 shows graphically the corrective action of the duriron anode in restoring the cathodic current efficiency to its initial value, and its effect upon throwing power. It will be noted that in four instances the solu-

Table II.

Comparative Characteristics of Three Recommended Cyanide Plating Solutions.

The operating conditions in all runs were uniform in the following respects:

Duration of run, 10 minutes. (For Cyanide "D," average of 10 tests during continuous run.)

Current density, 2.15 amp/dm.^{2}

Anodes of cast zinc, as previously described.

Origin of Formula	Cathodic Current Efficiency	Distribution: Percent of total Zinc deposited on			Average Voltage	Operating Temp °C
		Plate 1	Plate 2	Plate 3		
Bureau of Standards	89.0	54.0	21.5	12.5	5.9	36
Bureau of Standards .... plus 15 g/L. NaCN (1)	80.3	42.7	22.2	15.3	4.7	40
Roessler and Hasslacher Co.	(2) 43.4	19.1	13.5	10.8	4.7	45
Roessler and Hasslacher Co.	(2) 47.0	21.1	13.6	12.3	4.7	40
Cyanide "D" (Res. Lab. App. Chem.) (3)	83.0	37.7	26.0	19.3	1.6	40

(1) Formula (Blum, Bur. of Standards):

Zinc Cyanide	65	grams
Sodium Cyanide	20	"
Sodium Hydroxide	60	"
Water	1000	cc.

(2) Formula (Wernlund; Roessler and Hasslacher Co.):

Zinc Cyanide	60	grams
Sodium Cyanide	52.5	"
Sodium Hydroxide	15	"
Sodium Carbonate	30	"
Sodium Fluoride	7.5	"
Corn Sugar	7.5	"
Gum Arabic	1.1	"
Water	1000	cc.

(3) Formula Cyanide "D":

Sodium Cyanide	53.2	grams
Zinc Cyanide	59.2	"
Sodium Hydroxide	43.8	"
Sodium Carbonate	9.5	"
Aluminum Sulfate	4.7	"
Lignol	11.8	"
Water	1000	cc.

tion was restored to substantially initial characteristics by the use of the duriron anode.

A second factor affecting the stability of the solution is the amount of addition agent present. Since the addition agent undoubtedly deposits on the particles of zinc as soon as the plating phenomenon occurs, there will be a gradual diminution in the amount of addition agent. From evidence obtained in the 180-hour run, it was found that an addition of 1.5 gm. of addition agent lignol per K.W.H. of energy consumption, was apparently sufficient to maintain the solution in good order.

Although glue was found to function satisfactorily as an addition agent, lignol appeared to be better, and the latter also has the advantage over glue in cost.

At times it may become desirable to measure the exact operating characteristics of the bath, such as the current efficiency, and distribution. For this purpose, a small scale bath, such as is described in this paper, will serve very well. By this means, rapid determinations may be made by simply transferring a portion of the production solution to the small scale tank, and making a measured run with the set of three cathode plates.

C. Comparison of Cyanide Solution "D" with Two Other Recently Recommended Cyanide Solutions.

The papers of Wernlund[17] and by Blum[17] appeared after the work described in this paper was completed. Using the 3-section cathode, runs were made employing the baths recommended by these two authors. A comparison of the results with those with Cyanide "D" is given in Table II. The observed characteristics may be summarized as follows:—

Bureau of Standards Formula. This solution had the best current efficiency, but the poorest throwing power. Plates were uneven in color; that is, No. 1 was bright, but Nos. 2 and 3 were a dull gray. The voltage was comparatively high.

Formula of C. J. Wernlund. The current efficiency was comparatively low, but the throwing power was good. A uniform, bright deposit was obtained on all plates. The voltage was lower

[17] *Loc. cit.*

than with the Bureau of Standards solution. Considerable cathodic gassing was noted.

Formula of Research Laboratory of Applied Chemistry. The results presented are the average of 12 runs made during 180 hours, in which time the bath was in continuous operation, the stability of the solution being maintained by use, from time to time, of the duriron anode, as previously noted. While the current efficiency was slightly below that of the Bureau of Standards furmula the throwing power was far superior, being about the same as that of Wernlund's formula. The deposits were uniform and even in color, and the very low voltage gives a marked economy in power consumption over either of the two other solutions.

It should be stated that conclusion No. 4 on page 263 of Wernlund's paper to the effect that high free alkali always causes fouling of the anodes was definitely contradicted by the experiments of this laboratory. Langbein recommended the use of sodium carbonate, but the Bureau of Standards paper (No. 195) on page 17 says that carbonates tend to form coarse or striated deposits, and recommends the use of high free alkali. The latter observations are in accord with ours.

CONCLUSIONS.

1. Zinc plating baths, the principal constituents of which are sulphate, fluoborate, or zincate, show small throwing power, although satisfactory deposits may be obtained with sulphate baths when anode and cathode are plane and parallel to each other.

2. Alkaline cyanide baths, having the composition of solution 9 of this paper, show high throwing power, moderately high efficiency, very low voltage, and give continuously good results when operated under proper conditions.

3. The proper conditions for operating the alkaline cyanide bath (solution 9) continuously were determined and found to be as follows: C. D., 2 amp./dm^2; temperature, 40° C.; stirring, moderate; anode, composite of zinc and duriron, the duriron surface forming 30 percent of the total anode surface. The use of an addition agent is necessary. Glue is fairly satisfactory, but "lignol" was found to be a better and cheaper material.

BIBLIOGRAPHY.

Cowper-Coles, S. O., and Walker, B. W., Eng. Pat. 7145, April 10, 1894.

Heathfield, R., and Rawson, W. S., Eng. Pat. 16,105, August 23, 1894

Richter, K., Zeits. f. Elektrotechnik. u. Elektrochem., 1895, **2,** 79 and 98.

Cowper-Coles, S. O., J. Soc. Chem. Ind., 1896, **15,** 414.

Leitner, H., Eng. Pat. 1572, January 20, 1897.

Gabran, O., Elektrotechnik, Zeits., 1903, **24,** 937.

Amberg, R., Ber. 1903, **36.** 11, 2489.

Szirmay, I., and von Kollerich, L., Eng. Pat. 5448, March 3, 1903.

Kendall, E. D., U. S. Pat. 786,221, March 28, 1905.

G. Langbein & Company, Fr. Pat. 358,622, October 18, 1905.

Burgess, C. F., Electrochem. and Met. Ind., 1905, **3,** 17.

Price, T. S., and Judge, G. H. B., Faraday Soc. Trans., June 12, 1906.

Pawek, H., Eng. Pat. 8562, April 12, 1907.

Pfanhauser, W. and Fischer, F., Ger. Pat. 171,034, February 14, 1905.

Price, T. S., Faraday Soc. Trans., March 19, 1907.

Siemens and Halske, A. G., Fr. Pat. 375,140, February 28, 1907.

Goldschmidt, R., Rev. d'Electrochimie et d'Electromet., 1907, **1,** 276.

Foerster, F., Elektrochem. **14,** 153.

Lafond, J., L'Electricien, **36,** 87.

Marc, R., Z. Elektrochem., **19,** 431.

Snowden, R. C., Trans. Am. Electrochem. Soc. 1907, **11,** 121.

Tucker, S. A., and Thomssen, E. G., Trans. Am. Electrochem. Soc., 1909. **15,** 477.

Holland, A., Metal Ind., **11,** 522.

Ballegeer, E., Brit. Pat. 11,271, May 11, 1912.

Daft, L., U. S. Pat. 1,042,533, October 29, 1912.

Mazzucchelli, A., Atti Accad. Lincei, 1914, **23,** II, 503.

Watts, O. P., and Shape, A. C., Tr. Am. Electrochem. Soc., 1914, **25,** 291.

Pring, J. N., and Tainton, U. C., J. C. S. Tra., 1914, **105,** 710.

Proctor, Chas. H., Metal Ind., 1917, **15,** 149.

Eichstaedt, T. C., Metal Ind., 1919, **17,** 22.

Metal Industry, 1920, **18,** 478.

Pleadwell, W. B., Met. Ind., 1921, **19,** 323.

Barclay, Met. Ind., 1921, **19,** 159.

Blum, Wm. Liscomb, T. J., and Carson, C. M., Bur. of Stds., Tech. Paper 195, October 17, 1921; Monthly Rev., Am. Electroplaters' Soc., Nov., Dec., '18, and Apr., '19; Brass World, 1919, **15,** 6.

Wernlund, C. J., Trans. Am. Electrochem. Soc., 1921, **40,** 257.

DISCUSSION.

G. B. Hogaboom[1]: The authors have presented a very good paper and brought out some interesting points regarding zinc solutions. The plater, however, will give a different interpretation of the "throwing power" of a solution. That term is generally applied to the depositing of metal in deep recesses without the use of a special anode arrangement. The plating of the inside of a tube closed at one end where there can be no circulation of the solution is a good example. The difference in the throwing power of a nickel sulphate solution containing a chloride salt and one having a fluoride salt is well known. The former will throw into deep recesses with little difficulty, but the latter will not deposit metal in such places even if the solution is agitated.

C. H. Proctor[2]: The throwing power of a solution used in electroplating is largely due to its composition. The internal resistance of the solution may be low, yet the throwing power of the solution may also be low. It is possible by the use of a specially prepared zinc cyanide solution to throw zinc inside of a steel tube, as I have done with this sample I have in my hands, even though the inside of the tube is entirely out of the path of anodic reduction or influence.

W. Blum[3] and H. E. Haring[4]: This paper is of great interest because it is among the first that has included a statement of the principles of throwing power and actual measurements of this property in certain solutions.

Consideration of this subject has led to the formulation of certain principles of throwing power, which are similar to but more detailed than those stated by the above authors. We are now engaged in a study of their application. Our purpose in stating these principles in advance of making detailed experiments upon them is to secure discussion and if possible examples in which these principles do or do not apparently apply.

[1] Research Electroplater, Scovill Mfg. Co., Waterbury, Conn.
[2] Expert in Electrodeposition of Metals, Roessler & Hasslacher Chem. Co., New York City.
[3] Chemist, Bureau of Standards, Washington, D. C.
[4] Bureau of Standards, Washington, D. C.

As Mr. Hogaboom has pointed out, the question of definition is important here.

1. *Definition.* The throwing power of a plating solution when operated at a certain voltage or average current density may be defined in terms of (a) the weight or thickness of metal deposited on the least accessible part of a cathode, or (b) the ratio of the thickness on the most accessible, to that on the least accessible part of the cathode. The latter view is equivalent to defining throwing power as the ability to plate uniformly on the cathode surface, regardless of the current efficiency.

If, as seems most practical, this latter definition is accepted, it is important to note that uniform distribution may be secured either by increasing the amount of metal deposited on the least accessible part, or by decreasing the amount on the most accessible part. The latter effect is involved in those experiments by Horsch and Fuwa in which good throwing power (evidently defined implicitly by them in the latter sense) was secured in solutions of relatively low cathode efficiency.

2. The primary distribution of current on a cathode is determined by the relation of the effective resistances to different parts of the cathode, which relation is fixed by the dimensions of the electrodes and the cell and is independent of the solution. This distribution is secured only when (a) alternating current is used, or (b) there is no polarization. When the latter condition is realized, the solution has zero throwing power, *i. e.*, the current will be least uniformly distributed over the cathode surface.

3. Throwing power is a measure of the deviation of current distribution (or more strictly speaking, of the metal distribution) from the primary distribution as above defined. It is governed by

(a) The relation between cathode potential and current density.

(b) The cathode efficiency at any given current density.

(c) The conductivity of the solution.

(a) and (c) are involved in the explanation given by Pfanhauser, Foerster and by Horsch and Fuwa. The latter authors have based their conclusions on the assumption that in their experiments the cathode efficiencies were the same at different current densities. This assumption is hardly justified, especially in these experiments in which the average cathode efficiency was only 50 percent or less.

The effect of these factors on throwing power may be derived from a consideration of the potential drop through the bath, which may be resolved into (1) the anode potential, (2) the potential necessary to overcome the ohmic resistance of the solution, and (3) the cathode potential. For present purposes the anode potential may be considered as uniform and constant and therefore need not be discussed. If we assume that the entire cathode is at the same potential, (which is justified by the usual low resistance of the metals to be plated), the total potential from (but not including) the anode, to and including the cathode must be equal on all parts of the cathode. If the effective resistance to a point "a" on the cathode is greater than to a point "b", it requires a higher potential to overcome the resistance to "a" than to "b" and therefore the residual or cathode potential at "a" must be lower than at "b". The actual current density at the points "a" and "b" will then depend upon the shape of the cathode potential-current density curve for the solution in question. Many such curves are published in Foerster's "Electrochemie." These curves vary from the nearly vertical as, *e. g.*, with a lead fluosilicate solution to those approaching the horizontal, as, *e. g.*, with the copper cyanide solution. Nickel, zinc and copper sulphate solutions give intermediate curves. Consideration of these curves indicate that the most readily polarized solutions and hence those giving the flattest curves are the best throwing solutions. Since all of the curves tend toward the perpendicular with increasing current density it follows that low current densities should give better throwing power.

Increasing the conductivity of a given type of solution improves the throwing power unless it simultaneously causes the cathode

potential-effective current density curve to be more nearly vertical. The lower the e. m. f. required to overcome the ohmic resistances to two points on the cathode, the more nearly alike will be the residual or cathode potentials at these points and hence the current densities will be more nearly uniform.

A few experiments have indicated the validity of the above principles. Thus it has been found that agitation decreases throwing power, which is probably due to the reduction in cathode polarization (*i. e.,* excess potential above the equilibrium value) by the renewal of liquid at the cathode. An increase in temperature usually decreases throwing power. In such cases, it is apparent that the reduction in polarization caused by heating the solution is more significant than the simultaneous increase in conductivity.

It is probably possible to predict the effect of any change in composition or operating conditions upon the throwing power by determining the effect of such a change upon the cathode potential-effective current density curve. Such measurements are now in progress, together with actual measurements of the throwing power.

C. H. Proctor: We might define the throwing power where we want to deposit metal in deep recesses as internal throwing power. So a solution should be determined by its internal throwing power, not its external, because it is easy to prepare a solution whereby you can deposit on the outer surface the same as Mr. Hogaboom has mentioned, but the plater has many times thrown inside an article of considerable depth. You can examine this piece of tube and you will find that the zinc is thrown in, and yet the ends were not exposed to the anodes. Solutions that have low internal resistance, that is, requiring low voltage pressure, may also have a very low throwing power, so resistance and throwing power of a solution should not be confused.

W. G. Horsch: The discussion has been enlightening to one who has had no practical experience in electroplating. Referring to the points which have been raised. (1) I agree with Dr. Blum and the Chairman that definition always is very important;

(2) from the percent of the theoretical zinc deposited on any two plates as given by our curves it is a simple matter to calculate the ratio of zinc deposited and this has been done in Fig. 3; (3) that the current efficiency should be the same at all points of the cathode I agree is not rigidly true, but it probably is true enough to serve as an assumption for a theory which was to serve as a guide in experimental work; and (4) finally I agree with Mr. Hogaboom that the real test of any plating solution is the results it will give in practice.

A paper presented at the Forty-first General Meeting of the American Electrochemical Society held in Baltimore, Md., April 29, 1922, President Acheson Smith in the Chair.

HYDROGEN OVERVOLTAGE AND CURRENT DENSITY IN THE ELECTRODEPOSITION OF ZINC.*

By U. C. Tainton,†

If there be one factor, in the production of electrolytic zinc, which would seem to be firmly established, it is that relating to the necessity of a pure electrolyte. From Mylius and Fromm[1] onwards, the most gratifying unanimity prevails in the literature in this regard.

Laist[2] (*et al.*) says "pure solution is the greatest single factor in the production of electrolytic zinc." Hansen,[3] "impure solutions invariably yield imperfect cathodes." Hall[4] states "the requirement, and I use it in the singular, for zinc electrolysis, is zinc sulphate and zinc sulphate only." Siemens and Halske[5] "Every other metal and even carbon must be completely excluded."

These are high ideals. The production of pure zinc sulphate solution is no easy matter. The writer knows of one case in which a very pure zinc sulphate solution was produced (by Professor H. G. Stanley of the Transvaal School of Mines), and its preparation occupied several weeks. The production of pure zinc by electrolysis of this solution required considerable ingenuity, on account of the contaminating effect of the electrodes. Any anode that could be used dissolved to some extent in the solution. Again, it was found that the cathode on which the zinc was deposited always alloyed with it and prevented perfect purity.

Finally, however, the problem was solved by placing the anode in another vessel connected with the catholyte by a long tube full of solution. The cathode was just immersed in the solution and gradually raised as the zinc grew downwards, in the same way as is done in the preparation of metallic calcium. It is interesting to record that the zinc so produced possessed properties quite

* Manuscript received March 13, 1922.

†Bunker Hill and Sullivan Mining Co., San Francisco, Calif.

different from those usually ascribed to the metal. It did not tarnish in the air, it was practically unaffected by sulphuric acid of any strength, and it could be beaten out like gold leaf so that it transmitted light.

The solutions above mentioned were regarded by Professor Stanley as very nearly pure. He recognizd however the probability of some contamination—from the containing vessels, etc. It is needless to say that his standards of purity were very different from those of the manager of an electrolytic zinc plant who speaks of "pure" solution. In fact, considerable difficulty attaches to the mere definition of the word "pure" in this connection. The standard can not be one of freedom from all other metals because all commercial solutions contain substantial amounts of magnesium, sodium, calcium and manganese. Nor does it meet the case to say freedom from other metals electronegative to zinc, because the presence of cadmium is relatively unobjectionable (except from the standpoint of the production of Grade A zinc). Iron in limited amounts is not harmful. Mercury, it is said, is beneficial. (Lodge). Commercial solutions always contain a little copper and lead, as is shown by the analysis of the zinc, and usually traces at least of cobalt, arsenic, and antimony.

In defining purity of solutions, therefore, we are driven to some such standards as those inherent in Hansen's[3] statement—"The behaviour of the zinc cell is the best and surest check on the thoroughness of the purification methods used . . . . it also appears proper to accept such a cell as determining the purity of a solution."

Let us say then that a pure solution is one that will give a good deposit of zinc, with a high current efficiency in the zinc cell. It then remains to define the conditions of electrolysis, such as temperature, current density, nature of electrodes, circulation of solution, degree of acidity and thickness of deposit. A variation of any of these factors may vitally affect the quality of zinc that can be obtained from the solution in question. It should be remembered, for example, that under the conditions of Siemens and Halske's[5] work, the use of lead anodes was found hopelessly to contaminate the solutions; this is an interesting point to which reference will be made later.

The foregoing introduction will serve to bring out the point

that whereas commercial electrolytic zinc is commonly spoken of as being deposited from pure solutions, it is really, from an electrochemical standpoint, deposited from impure solutions, in which the impurities are of such nature and amount that the cost of further purification would not be balanced, under the particular conditions of electrolysis, by increased current efficiency.

It may be said indeed that the commercial production of electrolytic zinc is necessarily carried out in a solution containing impurities. Unless a diaphragm is used the presence of free acid is also axiomatic.

The phenomena connected with the deposition of zinc from such solutions are somewhat complex, and it is proposed here to consider some of the simpler aspects of the problem.

The theoretical voltage required to decompose water is about half that necessary to resolve zinc sulphate. It would therefore appear, on thermodynamic grounds alone, that the electrolysis of an acid zinc sulphate solution would result simply in the decomposition of water, with production of hydrogen only at the cathode. This does in fact occur when the electrode employed is, for example, of platinum black. It does not occur, however, at a cathode of pure zinc, which for some reason (we will not here discuss the nature of overvoltage) opposes considerable resistance to the evolution of hydrogen at its surface. If, however, there be present, or be deposited, at some point on the zinc surface, a particle of some metal, such as copper, at which the hydrogen overvoltage is low, there may be nothing to prevent the separation of hydrogen at that point.

We may notice here the fact that there is probably some minimum size which the spot of impurity must attain. It is unlikely, for instance, that separation of hydrogen bubbles could occur as the result of the deposition of a single molecule of cobalt. Probably a crystal or segregation of molecules must reach at least a certain size before becoming effective, and this would account for the fact that there seems to be a certain critical concentration for each impurity, above which it becomes dangerous. C. A. Hansen[3] "It has consistently appeared that a variation between 0.0003 and 0.001 gm. per liter of antimony made the difference between excellent and impossible cell room operation."

The deposition of solid metallic zinc therefore, resolves itself

into a problem of the continued maintenance, at all points of the cathode surface, of a high hydrogen overvoltage. In general those impurities would be expected to be most dangerous at which hydrogen overvoltage is lowest. A list of the values of the overvoltage of the different metals will illustrate this point.[6]

Mercury	0.78	Cadmium	0.48
Zinc	0.70	Copper	0.23
Lead	0.64	Nickel	0.21

If the values given above remained constant under all conditions, it would not be possible to deposit any zinc from an acid solution on to a surface, say, of copper. As the potential of zinc on the hydrogen scale is about 0.75 volt while the hydrogen overvoltage at copper is only 0.23 volt, it is evident that only hydrogen would separate. It must be remembered, however, that the overvoltage, as usually given, is the "zero current" overvoltage and that overvoltage increases with current density. Whether it increases sufficiently to reach the figure of 0.75 volt with any reasonable current density could not be determined with certainty from the literature. Some of the figures obtained by Tafel,[7] Foerster,[8] Newbery,[9] given in Table I, will serve to show the wide discrepancies that exist.

TABLE I.

Hydrogen Overvoltage Figures from Three Sources

Cathode	Foerster 116 Amp./sq. ft.	Tafel 93 amp./sq. ft.	Newbery 93 amp./sq. ft.
Zinc	...	...	0.71
Lead	1.35	1.30	0.59
Tin	1.16	1.15	...
Cadmium	1.23	1.22	...
Copper	0.79	0.79	0.38
Iron	...	...	0.27
Nickel	0.74	0.74	0.19
Antimony	...	...	0.43

Opinions on the subject being so diverse, it was decided to investigate the matter experimentally, using an electrolyte of the approximate composition employed in technical zinc electrolysis.

The object in view was to determine the existence or otherwise of a critical current density for the different metals. This critical current density might be defined as minimum current density which, for the given solution, would raise the hydrogen overvoltage of the given metal to the point at which deposition of zinc would begin.

The following procedure was employed. A cathode was made of the metal undergoing investigation, and electrolysis was carried out in carefully purified zinc sulphate solutions carrying free sulphuric acid. The applied current was gradually increased and the point at which the deposition of zinc commenced was noted.

TABLE II.

Critical Current Density

Cathode	Low Acid Electrolyte Amp. per. sq. ft.	High Acid Electrolyte Amp. per sq. ft.
Copper polished	9.3	18.2
Copper, etched	20.6	30.1
Carbon	2.3	6.9
Iron	104.8	233.0
Lead	1.5	3.0
Cadmium	6.7	4.6
Cobalt, electrolytic, rough	286.0	624.
Nickel, electrolytic	883.	1470.
Antimony, electrolytic	535.	1300.

In most cases, this point was very distinctly marked by the sudden cessation in the "gassing" around the electrode and the appearance of the bright zinc surface. Of course once a zinc surface is obtained, hydrogen will no longer separate, so a fresh electrode must be used for each experiment.

The cathode used was a rod, 0.5 in. diameter, having its lower end dipping inside a small cup. Precautions were taken to ensure a uniform distribution of current density. Determinations were made in two different solutions representative of existing practice, one a "low acid electrolyte" containing 26 gm. zinc and 75 gm. H_2SO_4 per liter, and the other a "high acid electrolyte" containing 36 gm. zinc and 260 gm. H_2SO_4 per liter. The results are shown in Table II.

The effect of the addition of a colloid (gelatin) was then studied. Results were somewhat irregular, but showed in general a fall in the critical current density with increasing concentration of gelatin up to a certain point, after which there was no further improvement or the critical current density increased again. The results for iron and nickel, which are typical, are plotted in the attached curve. Fig. 1. Evidently the presence of a colloid such as gelatin raises the hydrogen overvoltage for other metals in the same way as it has been found to do for zinc.[10]

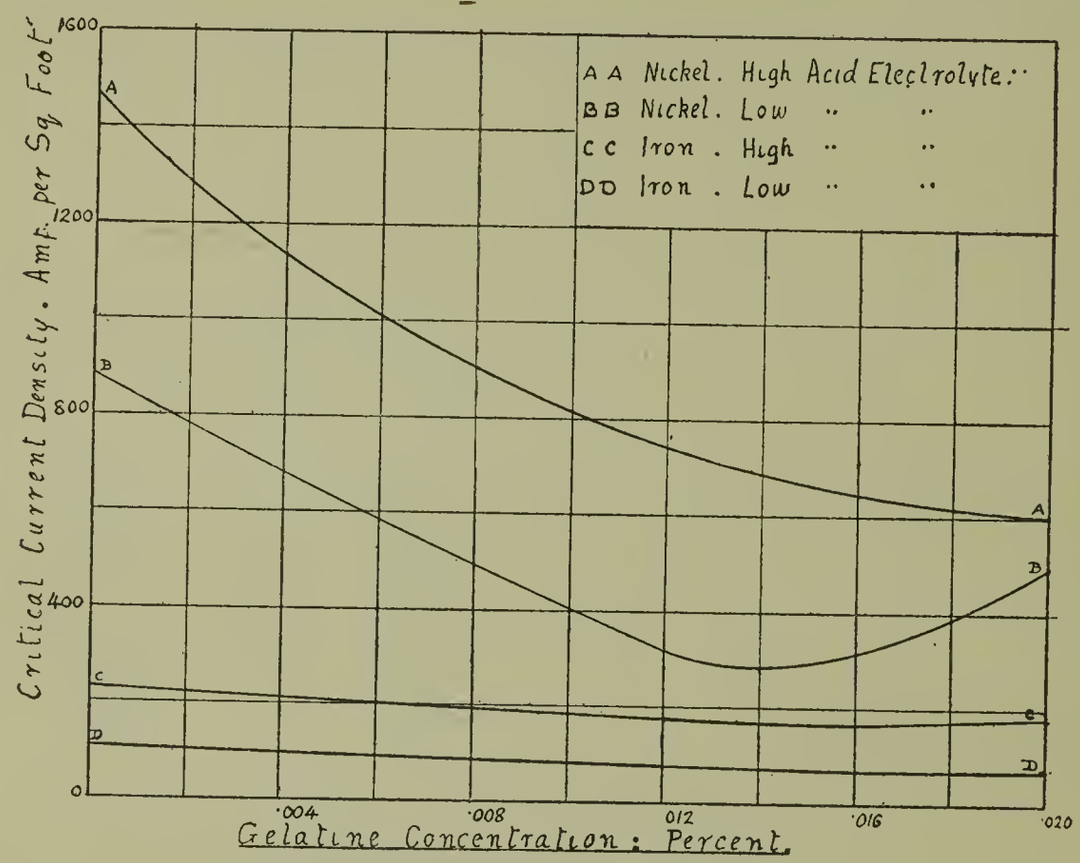


FIG. 1
Effect of Colloid on Critical Current Density for Nickel and Iron

The figures in Table II represent the average of a considerable number of tests. It is difficult to get results exactly concordant, because the overvoltage depends greatly on the previous history of the surface—degree of polish or acid attack as the case may be. The experiments demonstrate that for the metals investigated (and probably for all metals) the hydrogen overvoltage may, by sufficiently raising the current density, be made to exceed the potential of zinc, *i. e.*, about 0.75 volt on the hydrogen scale. This is at variance with the majority of figures obtained by means of the commutator method, and it would seem to place this method definitely out of court for measurements of this kind. This

point is emphasized because the author has himself made use of the commutator method in previous work[10] and now believes the standard electrode method (which was used alternatively) to give the more reliable results.

The figures accord pretty well with the observed results with regard to the relative "obnoxiousness" of the various impurities. It must be remembered, however, that this method of measurement takes no account of the relative tendencies of the impurities to deposit with the zinc. This is probably the explanation of the apparently anomalous positions of copper and iron, for example, as compared with their behaviour in the zinc cell.

It is evident that an impurity deposited with the zinc may come down either in the form of separate crystals (local segregations), or it may come down as an intimate alloy (solid solution) with the zinc.

In order to determine the behaviour of alloys in this respect, the critical current density experiments were duplicated for brass and antimonial lead.

Critical Current Density Amp. per Sq. Foot

Cathode		Low Acid Electrolyte	High Acid Electrolyte
Brass, polished, Cu 64; Zn 36.....		5.3	7.9
Antimonial Lead, Sb 8; Pb 92.....	polished	36.7	40.1
	etched	87.3	108.

It is clear that the critical current density lies between those of the two constituents in each case. The difference between the low and high acid electrolyte is however much less marked in the case of the alloys than in the case of the pure metals.

In the case of a commercial deposit of zinc, the quantity of metal actually alloyed with the zinc must be very small, and the overvoltage of the surface should therefore be relatively high.

It seems probable however that a zinc surface which has been corroded by acid will have a lower overvoltage and a higher critical current density than an uncorroded surface. To test this point, a zinc sulphate solution was prepared, as pure as conveniently possible, by adding excess of electrolytic zinc to chem-

ically pure sulphuric acid solution and precipitating iron, cobalt and manganese with zinc oxide and permanganate. This solution was acidified and electrolyzed, and after a good deposit of zinc had been obtained, the circuit was broken and the zinc allowed to redissolve. It would be more correct to say the zinc was given the opportunity to redissolve, because it showed no appreciable tendency to do so. It was found necessary to short circuit the cell by connecting the anode and cathode before any visible action could be observed. The corroded deposit was then tested for critical current density as above.

	Time subjected to Corrosion (short circuited) Minutes	Critical Current Density Amp. per sq. ft.
Pure zinc	10	19.6
	20	20.8
	30	67.3

The zinc in the above test was certainly not pure, because lead anodes were used for the electrolysis. On the other hand it was probably purer than any metal likely to be found in commercial practice. The results merely go to show that even a relatively pure zinc after being strongly attacked by acid possesses a low hydrogen overvoltage.

It was attempted to determine the critical current density of an electrolytic cobalt-zinc surface, formed by the electrolysis of a zinc sulphate solution containing cobalt in the proportions which might be encountered in practice (up to 150 mg. Co per liter). However so long as the zinc surface remained bright and uncorroded, no appreciable fall in overvoltage could be detected. This is in accordance with the observation that such solutions will always begin to give a good deposit of zinc even at low current densities, though the deposit may be attacked later.

A remarkable difference was observed however when these cobalt-zinc deposits were allowed to corrode in acid. No short circuiting was necessary in this case, as the deposit dissolved fairly readily in either cobalt-bearing or cobalt-free electrolyte. On again connecting the circuit, it was found necessary to apply high current densities before new zinc would deposit on the corroded surface.

Deposit from Solution Containing Co. Mg. per liter	Time redissolved Minutes	Critical Current Density of Corroded Deposit amp. per sq. ft.
150	5 (approx.)	1000
50	5	267
10	15	18.0

The results point clearly to the conclusion that the presence of cobalt in the zinc deposit does not perceptibly lower the overvoltage of the surface so long as the zinc surface is clean and growing, *i. e.,* the current density is sufficiently high. If however corrosion once begins at any point, the overvoltage of the corroded alloy is so low that no further zinc will deposit, and a hole will be formed which will tend continually to enlarge. This is in agreement with the observed facts.

The above experiments seem to throw some light on the rather vexed question of the manner in which impurities in the electrolyte operate to bring about corrosion of the deposit. Some investigators have attributed the effects to the increased "corrosive action" of the solution on the zinc surface. Deleterious results are noted, however, with quantities of impurity so minute that it is difficult to conceive that the chemical activity of the solution can have been greatly increased by their presence. For instance, Laist[2] says "Arsenic and antimony are particularly injurious, causing very poor current efficiencies and small yield per horsepower when present in amounts so small as almost to defy detection—one milligram or less per liter."

It seems impossible that such minute amounts of arsenic could increase the "corrosive action" of the solution to the extent observed. On the contrary, it is well known that the presence of arsenic in sulphuric acid reduces its corrosive action on iron or steel. It is difficult therefore to believe that one milligram per liter of arsenic (not ordinarily very active chemically) could increase the chemical activity of a solution more than say a hundred milligrams of ferric sulphate, permanganic or chromic acid.

Other investigators again have regarded the effects of impurities as being due to "galvanic couples" formed by the particles of impurity on the surface of the zinc. According to this view, the deleterious effect of any impurity would be determined by its

position in the electrochemical series, the greater the E. M. F. of the galvanic couple, the greater being its effect in causing corrosion.

This however is not, except in a very general sense, found to be the case. For instance, nickel which stands relatively high in the series is one of the worst impurities, whereas mercury which is almost at the bottom of the scale is actually beneficial.

Nor does it meet the case completely to say that the hydrogen overvoltage of the impurity is the determining factor. For one thing the impurity, if deposited with the zinc at all, is often deposited in only extremely minute quantities. Laist[2] says "The presence of antimony in the zinc deposit has not been detected, although present in the electrolyte in considerable quantities." Hansen[3] says "On the other hand, since zinc is electropositive to all of the impurities with which we have been concerned, if one collected the last remains of a rapidly corroding deposit one should expect to find the impurities concentrated in that fraction. Yet when only a black scummy residue is all that is left of the deposit that scum is invariably lead and copper. The causative impurities are not detectable, or barely detectable, in the residue."

A further difficulty in the way of regarding the phenomenon as wholly due to the low overvoltage of the impurities themselves lies in the fact that some of the impurities which are particularly objectionable do not have correspondingly low hydrogen overvoltage. Arsenic for example has a relatively high hydrogen overvoltage, and as shown by Watts[18] it is by virtue of this effect that the presence of arsenic reduces the corrosive action of sulphuric acid on iron.

These difficulties may be reconciled if the variation of hydrogen overvoltage with current density be taken into account. On this theory the worst impurities would be those which show the least increase of overvoltage with increase of current density, or in other words which interpose the least resistance to the liberation of large amounts of hydrogen per unit of area. It is noticeable by the way that the most obnoxious impurities As, Sb, Co, Ni, are those which have the power of combining with or occluding hydrogen and perhaps so catalyzing the production of gaseous from atomic hydrogen.

The experimental results above outlined fit in very well with this

theory. Antimony is indicated to be the most active of all common impurities, an expectation which is fully confirmed in practice. To obtain some idea of the quantity of antimony which might be effective (according to this theory) a high grade zinc cathode, containing 0.03 Pb and 0.05 Cd, was melted into a small ingot and compared with another ingot, similar in all respects except for the addition to it of 0.01 percent Sb (20 mg. Sb in 200 gm. Zn). The two ingots were immersed in 10 percent H_2SO_4 for two hours and the loss of weight determined. The sample No. 2 containing antimony was attacked rather more rapidly at the outset, but the difference was not remarkable until the bright surface of the cast zinc turned black. Then the solution of the antimony zinc became extremely rapid while the other sample (which remained bright) was attacked only very slightly. Sample No. 1 lost 0.048 gm. Sample No. 2 lost 48.2 gm. approximately 1000 times as much.

It is clear that the presence of a minute trace of antimony to the zinc may bring about a surprising reduction in hydrogen overvoltage. Whether the effect is due to the low overvoltage of antimony itself, or to a modification in the molecular structure of the zinc, presents an interesting field for speculation in which the bulk of the evidence would seem to support the latter view.

The important point to remember lies in the fact that the presence of these various impurities does not greatly lower the hydrogen overvoltage of a bright zinc surface. It is only after being attacked by acid that the bad effects become so strikingly apparent. An explanation is here suggested for the fact that earlier workers in Germany and elsewhere found the use of lead anodes entirely inadmissible. Siemens and Halske and Ferchland[5] reported that their pure zinc sulphate solutions would give excellent deposits with anodes of precipitated manganese dioxide. Immediately lead anodes were substituted, trouble was experienced with the corrosion of the deposits.

It has always been somewhat of a mystery as to why this effect was not observed in the later commercial development of electrolytic zinc in this country. The fact that Siemens and Halske used current densities only about one half those now used gives the clue to the probable explanation. When lead anodes are used, lead is always deposited with the zinc either mechanically or from solution, and the question of whether this

lead will bring about corrosion of the zinc will depend on the applied current density. If it exceed the critical current density of the lead (as previously defined) at all points the zinc will continue to plate over it. Otherwise local corrosion will commence at points of low current density.

A somewhat similar point arises in connection with impurities in the aluminum starting sheet. Laist and Elton[12] have recorded an observation that impure aluminum was found under certain conditions to bring about resolution of the zinc. Copper is mentioned as being especially harmful. It is evident that, at low current densities, the presence of a particle of copper on the aluminum would cause the evolution of hydrogen at that point right from the beginning of electrolysis. These hydrogen bubbles would (unless the contact angle was artificially lowered) adhere to the surface, and prevent the deposition of zinc, thus causing the formation of a crater at that point. Eventually this crater would become so deep that resolution of the deposited zinc would begin, and once started it would tend to spread over the surface. This effect of course would not be observed at higher current densities because the overvoltage of the impurities would be raised to such a point that zinc would plate over and bury them, after which the cathode surface becomes one of zinc only.

An important phase of the interdependence between current density and overvoltage arises in connection with the possible thickness to which deposits can be carried. It is a matter of general experience that the current efficiency of a zinc deposit is at a maximum at the start, and falls continually as electrolysis proceeds. This fall in efficiency may be fast or slow—in very impure solutions the efficiency may fall to zero within a few hours—but in any case it sets the limit to which deposits can with economy be carried. It is possible that in absolutely pure solutions the slope of the current efficiency-time curve would be so slight as to be negligible; but no investigation of this case is on record. The difficulties connected with the production of pure zinc sulphate solution are sufficient to deter most people from attempting the problem.

In the "commercially pure" (Hansen) solutions of technical zinc practice, we have to deal with a cathode which operates at first at high current efficiency; in which the current efficiency

continually falls, ultimately (if electrolysis be long continued) crosses the zero line and becomes negative; *i. e.,* the zinc redissolves.

It is evident then that there exists some factor or set of factors which give to an old cathode surface a lower current efficiency than to a new one. Speaking generally, we may say that the average hydrogen overvoltage of a zinc cathode tends to fall with time, and those conditions which would tend to uphold and maintain that overvoltage would be those most favorable to the formation of good zinc deposits.

First among the causes of the fall in current efficiency is the roughening of the cathode surface. From the first moment of electrolysis there is a continual increase of surface, continual decrease of current density, and consequently continual fall in overvoltage. The formation of trees, craters, etc., gives rise to local spots of low current density, and when the overvoltage at these points falls below the critical protective value, deposition of zinc ceases and local corrosion sets in.

The appearance of a zinc deposit which has suffered corrosion of this kind is often rather remarkable. A common variety is one in which the deposit appears almost perfect from the front side but when viewed from the starting sheet side, shows small holes irregularly distributed, sometimes only two or three to the square foot, and showing in the walls of the hole the black color characteristic of impure zinc that has been attacked by acid. The holes are frequently much larger in diameter at the back of the cathode than at the front (Hansen[3]).

In such a case, it is clear that the hole has been eaten away in zinc already deposited. Often it is possible to find local defects in the surface of the cathode, which give rise to points of lowered current density, which in turn give the acid opportunity to attack the zinc. Sometimes it is a depression in the aluminum surface, sometimes a projection. The latter gives rise to growth of a "tree" which lowers the current density of the cathode surface in its immediate vicinity. In Fig. 2, is shown a photograph of a cathode deposit from a solution high in cobalt. The zinc has been cut through to show in section a hole of the kind mentioned. The small tree on the face which led to the lowering of the current density is clearly seen. Behind it is a cavity approximately spheri-

cal in shape and extending right through the deposit to the face of the starting sheet. The small inequality in surface which gave rise to the growth of the tree was clearly visible on the aluminum cathode.

It must not be assumed, however, that irregularities in the starting sheet are to any considerable extent the fundamental cause of roughness of the deposit. The substitution of smooth sheets for rough ones might postpone, but would not remedy, the trouble. In fact, the condition of a growing zinc deposit as regards its smoothness of surface is essentially one of unstable equilibrium. There are almost no "levelling influences." Slight depressions rapidly become deep craters. Minute prominences quickly grow into "trees."

FIG. 2. (x1.5)
Section through Zinc cathode containing cobalt, showing single corrosion hole due to local lowering of current density.

There are several factors which tend to bring about this result. Take, for instance, the question of the adhesion of hydrogen bubbles to the zinc surface. In zinc sulphate solutions containing free acid and impurities, some hydrogen is always evolved simultaneously with the deposition of the zinc. These hydrogen bubbles tend to adhere to the zinc surface, and prevent the deposition of the zinc at the points which they touch. The bubbles stick to the plate, especially at points of slight depression and the zinc builds round them, making it more and more difficult for them to detach themselves. Eventually the crater thus formed becomes so deep that it is continually occupied by hydrogen bubbles and the current density at the bottom of the crater is practically zero. This is a condition which in "impure solutions" leads frequently to the formation of corrosion holes in the deposit.

The size to which hydrogen bubbles will grow before disengaging is a function of the interfacial tension between the cathode

and the electrolyte, and may be roughly quantified by measuring the contact angle of the bubble at the solid liquid interface. For solutions free from colloids or organic substances, this interfacial tension is high, and the adhesion of the bubble very pronounced. It may be further increased by coating the cathode with a film of oil or adding a soluble oil (a fraction of one percent is sufficient) to the electrolyte. In this case, the experiment is of theoretical interest only as the adhesion of the bubbles is so great that the zinc deposit resembles a honeycomb, the zinc being deposited only in the spaces between the bubbles.

The converse case, that of the reduction of the contact angle by addition of some colloidal addition agent is, however, of great technical importance. A zinc solution free of colloid is something by no means easy to obtain, even in the laboratory, as the silicic acid derived from glass vessels functions as a colloid. A carefully purified zinc sulphate solution gave, when free acid was present, a porous deposit of the type shown in (A) Fig. 3. The addition of a small quantity of gelatin changed the character of the deposit to that shown in (B). An inspection of the two deposits leaves no doubt that the principal cause of difference lies in the differing adhesion of the hydrogen bubbles.

Below are shown some results obtained by Yu Hwa Twan[13] on the effect of gelatin on the contact angle of the hydrogen bubble at a mercury surface in $N/10$ sulphuric acid.

Percent Gelatin	Angle of Contact Degrees
0.0	90-85
0.00133	75
0.00266	70
0.00533	70-65
0.01333	60-50

At higher gelatin concentrations bubbles would not adhere to the mercury surface, and measurement of the contact angle by this method became impossible.

We come now to the other main cause of rough deposits, the growth of "trees." (The word is used generically to denote all projections, knobs, warts, ridges, arborescent or dendritic deposits, *et hoc genus omne.*) Once a tree starts, it is evident that it will tend continually to increase in size on account of its greater cur-

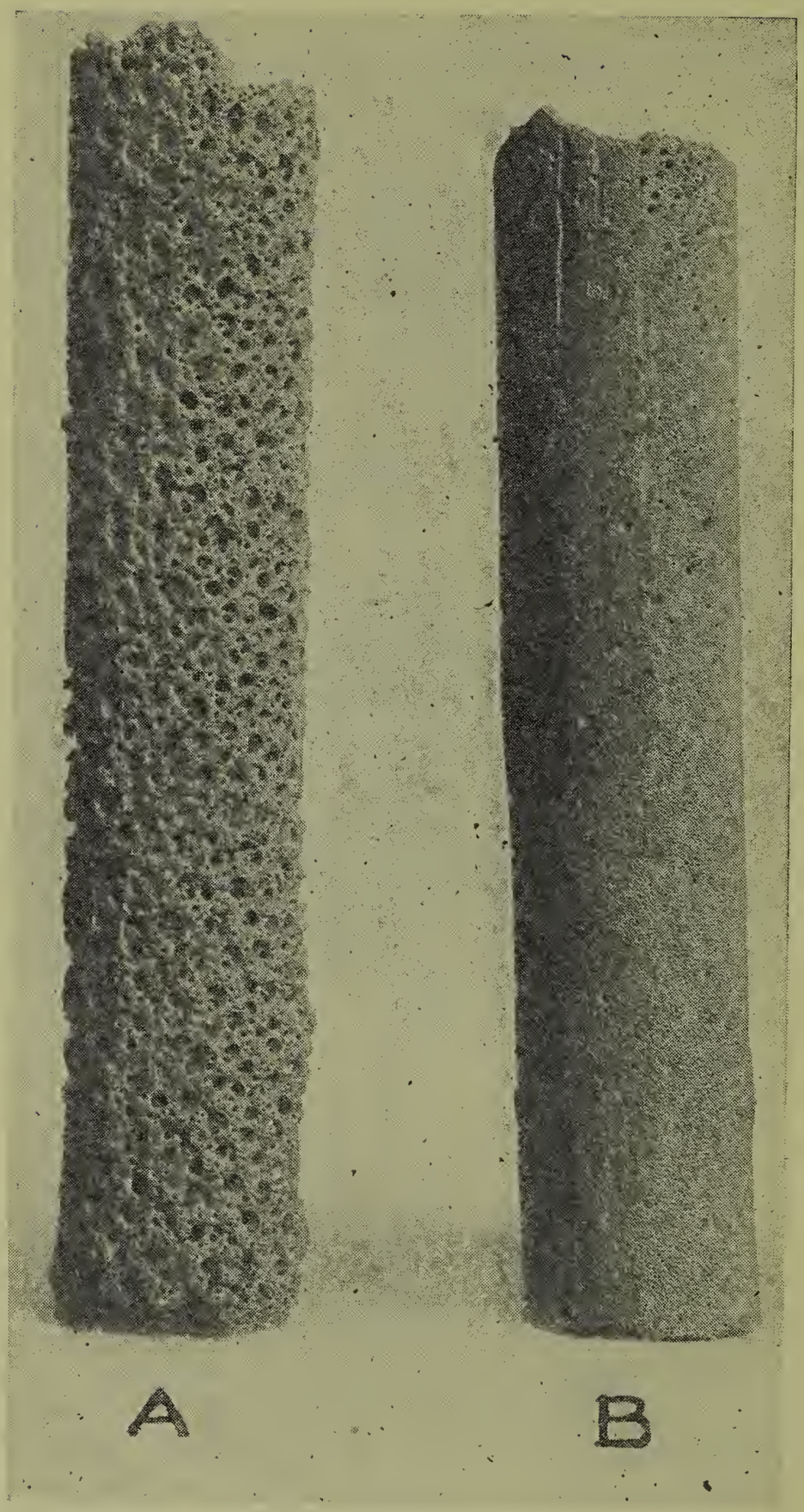


FIG. 3. (x1.5)

(A). Zinc deposit from well purified solution, almost free from colloid, showing effect of adhering hydrogen bubbles.

(B). Zinc deposit from same solution but with trace of gelatin added.

rent density and its contact with richer solution. The main factors affecting the growth of trees are as follows—

1. Potential-gradient in the layer of electrolyte bounding the cathode. This is a function of current density and conductivity of electrolyte.

2. Circulation of solution.

3. Size of crystals of metal deposited from solution.

Regarding the first mentioned factor it is commonly observed that the more acid a solution contains, the smoother is the zinc deposited from it. Hansen[3] states "all deposits made at above 100 gm. per liter acidity are reasonably smooth at all current densities up to 100 amp. per sq. foot within the writer's experience."

With reference to the circulation, the beneficial effect on the deposit of a rapid movement of the electrolyte past the cathode is a general rule of electrochemistry. It is made use of in many analytical separations to secure dense, adherent deposits. It forms the basis of the Cowper-Coles[41] process for the electrolytic deposition of copper tubes. It helps to explain the exceptionally fine zinc deposits obtained by revolving disc cathodes of the Hoepfner type; though in this case it is probable that the breaking of adhering hydrogen bubbles as the cathode leaves the solution is of more importance than the movement through the electrolyte.

Exactly how the movement of the electrolyte past the cathode operates to prevent tree formation is not quite clear. It may perhaps be regarded as a mechanical action, due to the friction of the solution acting in much the same way as travelling rubbers of agate or sheepskin act on copper deposits. (Elmore,[15] Julien and Dessolle.[16]) Borchers[17] recommends a rapid upward movement of electrolyte past the face of the cathode in order to detach hydrogen bubbles. He mentions the fact that if a downward movement of the electrolyte be artificially produced, the hydrogen bubbles cannot dislodge themselves and zinc is obtained consisting entirely of hollow shells surrounding bubble holes.

When a high current density is used, the difference in density between the main body of the electrolyte and that in contact with the cathode surface becomes very pronounced and the upward streaming movement of the electrolyte is relatively rapid. This therefore acts as a smoothing influence on the deposit. It is fre-

quently noted that deposits are smoother at the top of the plate than at the bottom, and it is probable that this is an effect due in part at least, to the more rapid movement of the solution at the top of the cathode.

The close relationship between size of crystal deposited and growth of trees on the cathode is one that needs no elaboration. Solutions such as lead nitrate or stannous chloride which yield a highly crystalline deposit invariably give rise to heavy tree formation. Complex ions such as the double cyanides or oxalates usually give very small fine crystals, and are in consequence employed in plating work where smoothness of deposit is of major importance. It is possible that the beneficial effect of colloids in obtaining smooth deposits is due partly to the suppression of the crystalline form and consequent discouragement of tree formation.

It is possible also that another beneficial effect of the colloid may arise from its function in preventing the segregation of deposited impurity in crystals at definite spots on the cathode surface. In the presence of the colloid the impurity is perhaps uniformly distributed through the deposit as a solid solution in the metal and thus offers less opportunity for local corrosion points due to low hydrogen overvoltage.

We may quote here some remarks of W. E. Hughes,[19] which appear apposite. "It has been stated that the employment of colloids in baths used to deposit metal electrolytically should be avoided. Any such general statement is regrettable since it is unsupported by facts." In fact the employment of colloid in the zinc cell rests on a sound scientific basis. It tends to raise the overvoltage of hydrogen both at a zinc surface and at surfaces of other metals—a point of especial importance since all commercial solutions contain relatively considerable quantities of impurities. It lowers the contact angle of the hydrogen bubble, thereby facilitating its detachment from the face of the cathode and promoting the smoothness of the deposit. It restricts the crystalline growth of the metal and thus restrains the formation of "trees," which otherwise form rapidly and by increasing the surface area lower the current density, and consequently the hydrogen overvoltage of the whole surface.

We find, therefore, the following conditions indicated as

favorable to the production of good zinc deposits from impure, acid solutions:

1. High current density. This gives high overvoltage of hydrogen.

2. High electrolyte conductivity. This permits a low potential gradient and restrains "trees," which lower current density.

3. Diminished interfacial tension at contact surface of cathode and electrolyte. This gives a small contact angle preventing the hydrogen bubbles from adhering to cathode.

4. Rapid upward movement of electrolyte past cathode surface. This usually arises automatically if sufficiently high current densities be employed.

5. Presence of some addition agent which will restrain crystalline growth of cathode deposit and raise overvoltage of impurities.

It will be noted that the last four points are all directed towards maintaining the smoothness of the deposit and so retaining the benefit of the first condition, namely, high current density.

From a theoretical standpoint it would be best to combine the conditions mentioned above with a low acid concentration. But such a combination is technically impossible on account of the low conductivity of such solutions. Unless the conductivity is high, the deposit rapidly becomes rough, and this lowers the current density. Also the use of high current densities with low acid solutions would be commercially impracticable on account of the high terminal voltage required. As a matter of practical economy, applied voltage should not exceed at most 3.75 volts per cell. This is easily obtained at 100 amperes per square foot if the acid strength be above 200 gm. per liter. But at 50 gm. H_2SO_4 per liter the necessary voltage for the same current density would be nearly twice as great.

The foregoing theory may help to account for the apparently anomalous results recorded by Dr. J. N. Pring and the writer;[10] that if the free acid strength and the cathode current density be simultaneously increased to very high values, especially in the presence of a colloid, exceptionally good zinc deposits and high current efficiencies are obtained, even if the electrolyte contains relatively considerable quantities of impurities.

We find in general that the higher the acid strength in the electrolyte the better the quality of the zinc deposits obtained. Indeed, the zinc obtained in the higher acid ranges presents an entirely different aspect from "low acid" zinc, being much more compact and denser, often having the appearance of rolled or cast zinc.

It is rather difficult to give an accurate idea of the nature of deposits, so obtained, by photographs. In Fig. 4 is shown a corner broken from a cathode deposit, which indicates the smoothness of the surface and also the density of the structure. This deposit was obtained in plant operation from solution containing 250 to 280 gm. free sulphuric acid per liter, and 40 to 60 gm.

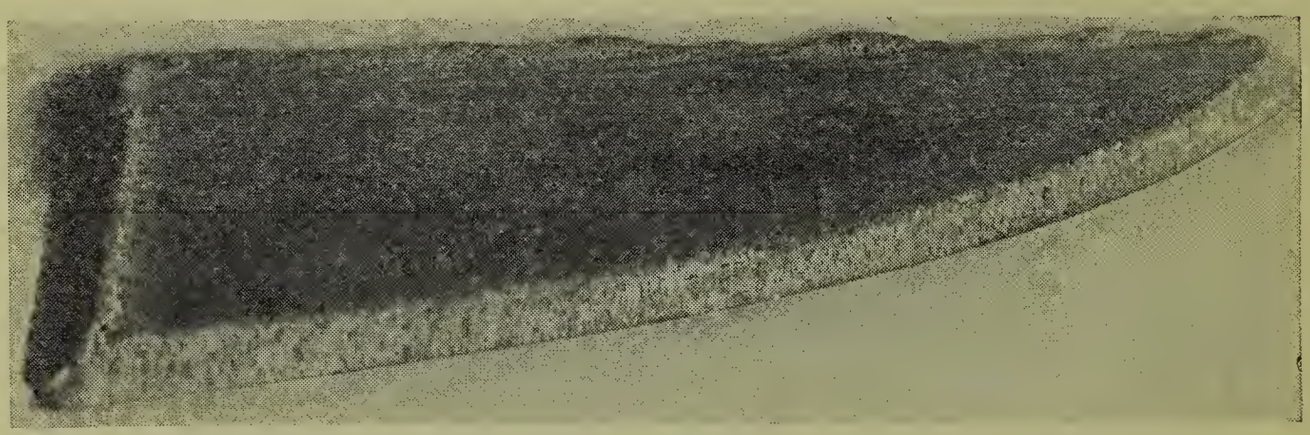


Fig. 4.
Corner broken from zinc cathode showing extreme smoothness and density of deposit under high acid, high current density, and colloid conditions. (Full size).

zinc per liter. Feed solution to the cells contained about 4.5 gm. per liter Mn and the following impurities:

Iron	256 mg. per liter
Arsenic	12.4 mg. per liter
Cobalt	8.5 mg. per liter

Current density 100 to 110 amp. per sq. ft. Colloid was used (glue) to the extent of about 3.4 pounds per ton of zinc deposited. Terminal voltage 3.5, current efficiency 90.5 percent, power consumption 1.44 K. W. H. per pound of zinc deposited.

SUMMARY.

1. Commercial electrolytic zinc is deposited from solutions which, from an electrochemical viewpoint, are to be regarded as necessarily impure and containing free acid.

2. The continued deposition of metallic zinc from such solutions depends on the maintenance of a high hydrogen overvoltage at all points of the cathode surface. This is attained by the maintenance at all points of a substantial current density, which, in turn, depends largely on the smoothness of the deposit.

3. By sufficiently increasing the current density the hydrogen overvoltage for all metals examined (lead, cadmium, copper, iron, nickel, cobalt, antimony,) may be made to exceed the potential of zinc on the hydrogen scale. This does not accord with figures obtained by the commutator method of measuring the variation of hydrogen overvoltage with current density, and it is believed that this method is unreliable.

4. The overvoltage of the alloys examined lies between the overvoltages of their constituents. In the case of zinc deposits containing impurities, the overvoltage is very high as long as the zinc surface is clean and growing. However, the overvoltage of an impure, corroded zinc surface is found to be very low, and so once corrosion begins (at a point of low current density), it tends continually to spread.

5. The function of colloidal matter such as gelatin in the electrolyte is to raise the overvoltage of hydrogen. It also lowers the contact angle of the hydrogen bubble, thus preventing adhesion of bubbles to the cathode surface. It tends to restrain crystalline structure of the deposit. All these factors tend to maintain smoothness of deposits.

6. Practical work indicates optimum conditions to be a free acid concentration of about 250 to 300 gm. per liter with a current density of about 100 amp. per sq. ft., and the presence of a minute quantity of gelatin or similar colloidal matter in the solutions.

ACKNOWLEDGMENTS.

The writer acknowledges cordially the assistance of Dr. J. N. Pring in advice and discussion; of Mr. L. T. Leyson, in the practical development of the above mentioned principles; and of Mr. H. E. Keyes, who performed the greater part of the measurements and experimental work. The latter gentleman, in conjunction with Dr. Tartar, of the University of Washington[20]

has since extended these experiments in a way such as to justify fully the doubts here expressed as to the accuracy of the commutator method of overvoltage measurement.

REFERENCES

1. Mylius and Fromm, Zeit. Anorg. Chem., 1895, **9,** 164.
2. Laist, Frick, Elton, Caples, A. I. M. E., 1920, **64,** 747.
3. Hansen, A. I. M. E., 1919, **60,** 206.
4. Hall, A. I. M. E., 1917, **57,** 709.
5. Siemens Halske, Br. Pat. 24806, 1906; Metall. 1910, **7**, 1.
6. Caspari, Zeit. Phys. Chem., 1899, 89.
7. Tafel, Zeit. f. Chem., 1904, 712.
8. Foerster, Zeit. f. Elektrochem., 1904, 715.
9. Newbery, Jour. Chem. Soc., **105,** 710.
10. Pring and Tainton, Jour. Chem. Soc., **105,** 710.
11. Ferchland, Br. Pat., 24806, 1906.
12. Laist and Elton, U. S. Pat. 1255433, 1918.
13. Yu Hwa Twan, Thesis University Calif., 1914.
14. Cowper, Coles, Electr., 1908, **61,** 680.
15. Elmore, Electrochem. and Metall., 1903, **3,** 150.
16. Julien and Dessole, Fr. Pat. 369746, 1906.
17. Borchers, Electric Smelting and Refining.
18. Watts, Trans. Am. Electrochem. Soc., 1912, **21,** 337.
19. Hughes, Physics and Chemistry of Colloids, Trans. Faraday Soc., 1920.
20. Tartar and Keyes, Jour. Am. Chem. Soc., 1922, **44,** 557.

INDEX

PAGE

Acidity of Nickel Depositing Solutions, The—M. R. Thompson.....333
Addicks, Lawrence—*Discussion* .....196 *et seq.*
Allan, Wm. G.—The Electrolytic Generation of Hydrogen and Oxygen with Special Reference to the Utilization of Off-Peak Power..239
Alternating Current in Direct Current Electrolysis, Experiments with—W. B. Jones 151
Alternating Operations, Intermittent and. Electric Furnace Iron and Steel—W. E. Cahill 99
Anderson, R. J.—*Discussion* 40
Annual Report of the Board of Directors..... 8
Annual Report, Secretary's 9
Annual Report, Treasurer's 12
Blum, Wm., and H. E. Haring—*Discussion*.....384 *et seq.*
Blum, Wm.—*Discussion*.....148 *et seq.*, 197, 198, 330, 360 *et seq.*
Board of Directors, Annual Report of..... 8
Booth Rotating Electric Furnace, The Melting of Cast Iron in the—H. M. Williams and T. B. Terry..... 87
Brown, O. W., and J. C. Warner—Electrolytic Preparation of Ortho-Amidophenol 225
Cahill, W. E.—*Discussion* 107
Cahill, W. E.—Electric Furnace Iron and Steel. Intermittent and Alternating Operations 99
Carburization in the Manufacture of Synthetic Cast Iron, A Study of —Clyde E. Williams and C. E. Sims..... 63
Carnotite Ores and Other Products of Low Activity, A New Method of Determining the Radium Content of—Victor F. Hess.....287
Cast Iron as Produced in the Electric Furnace, and Some of its Problems—George K. Elliott 21
Cast Iron, The Melting of, in the Booth Rotating Electric Furnace—H. M. Williams and T. B. Terry..... 87
Cast Iron, Synthetic, A Study of Carburization in the Manufacture of —Clyde E. Williams and C. E. Sims..... 63
Cast Iron, Synthetic—Jas. L. Cawthon, Jr..... 45
Cawthon, Jas. L., Jr.—Synthetic Cast Iron..... 45
Chang, M. Y., and Edward F. Kern—Conductivity of Copper Refining Electrolytes 181
Citizen, The Technical Man as a—Acheson Smith..... 15
Committee on Publications, Report of..... 4

PAGE
Comparison Between Shaft and Open Top Furnaces in the Manufacture of Pig Iron Electrically from Iron Ore, A—R. C. Gosrow..109
Conductivity of Copper Refining Electrolytes—Edward F. Kern and M. Y. Chang 181
Copper Refining Electrolytes, Conductivity of—Edward F. Kern and M. Y. Chang 181
Corrosion by Electrolyte Concentration Cells—Robert J. McKay.....201
Current Density in the Electrodeposition of Zinc, Hydrogen Overvoltage and—U. C. Tainton.....389
Current Efficiency of Zinc Plating Solutions, A Study of the Throwing Power and—W. Grenville Horsch and Tyler Fuwa.....363
Davis, Clark E.—*Discussion*.....145 *et seq.*
Depositing Solutions, Nickel, The Acidity of—M. R. Thompson.....333
Direct Current Electrolysis, Experiments with Alternating Current in —W. B. Jones 151
Effect of Impurities on Storage Batteries, A Study of—Helen C. Gillette 217
Electric Furnace, Booth Rotating, The Melting of Cast Iron in the—H. M. Williams and T. B. Terry..... 87
Electric Furnace, Cast Iron as Produced in the, and Some of Its Problems—George K. Elliott 21
Electric Furnace in the Iron Foundry, The—Lyman C. Judson and Harry P. Martin 127
Electric Furnace Iron and Steel. Intermittent and Alternating Operations—W. E. Cahill 99
Electric Furnaces, Electromagnetic Motions in—Carl Hering.....303
Electric Lamps, Vacuum Type, The Measurement of Pressures in—Duncan MacRae 311
Electric Pig Iron, Synthetic and, Sanely Considered—Robert Turnbull. 59
Electrodeposited Metal, Idiomorphic and Hyp-Idiomorphic Structures in—W. E. Hughes 317
Electrodeposition of Zinc, Hydrogen Overvoltage and Current Density in the—U. C. Tainton.....389
Electrolysis, Direct Current, Experiments with Alternating Current in—W. B. Jones 151
Electrolyte Concentration Cells, Corrosion by—Robert J. McKay.....201
Electrolytes, Conductivity of Copper Refining—Edward F. Kern and M. Y. Chang 181
Electrolytic Generation of Hydrogen and Oxygen with Special Reference to the Utilization of Off-Peak Power—Wm. G. Allan....239
Electrolytic Preparation of Ortho-Amidophenol—O. W. Brown and J. C. Warner 225
Electromagnetic Motions in Electric Furnaces—Carl Hering.....303
Elliott, George K.—Cast Iron as Produced in the Electric Furnace, and Some of its Problems..... 21

PAGE

Elliott, G. K.—*Discussion*.....38, 40, 84 *et seq.*, 97, 105 *et seq.*
Experiments with Alternating Current in Direct Current Electrolysis —W. B. Jones 151
Feild, A. L.—*Discussion*.....213, 215, 316, 360 *et seq.*
Fink, Colin G.—*Discussion*.....84, 179 *et seq.*, 211 *et seq.*, 273 *et seq.*
FitzGerald, F. A. J.—*Discussion*.....121
Forty-first General Meeting, Members and Guests Registered at the.. 13
Forty-first General Meeting, Proceedings of..... 1
Fuwa, Tyler, and W. Grenville Horsch—A Study of the Throwing Power and Current Efficiency of Zinc Plating Solutions.....363
Generation, Electrolytic, of Hydrogen and Oxygen with Special Reference to the Utilization of Off-Peak Power—Wm. G. Allan...239
Gillette, Helen C.—A Study of Effect of Impurities on Storage Batteries 217
Gosrow, R. C.—A Comparison Between Shaft and Open Top Furnaces in the Manufacture of Pig Iron Electrically from Iron Ore....109
Graham, A. K.—*Discussion* 360
Graham, Walter—*Discussion* 121
Haring, H. E., and W. Blum—*Discussion*.....384 *et seq.*
Hering, Carl—*Discussion* 273
Hering, Carl—Electromagnetic Motions in Electric Furnaces.....303
Hering, Dr. Carl, Made an Honorary Member..... 2
Hess, Victor F.—A New Method of Determining the Radium Content of Carnotite Ores and Other Products of Low Activity.....287
Hodson, Frank—*Discussion*.....83, 104 *et seq.*, 120, 124 *et seq.*
Hogaboom, G. B.—*Discussion*.....215, 359 *et seq.*, 384
Honorary Member, Dr. Carl Hering Made an..... 2
Horsch, W. G.—*Discussion*.....387 *et seq.*
Horsch, W. Grenville, and Tyler Fuwa—A Study of the Throwing Power and Current Efficiency of Zinc Plating Solutions.....363
Hughes, W. E.—*Discussion* 332
Hughes, W. E.—Idiomorphic and Hyp-Idiomorphic Structures in Electrodeposited Metal 317
Hydrogen and Oxygen, The Electrolytic Generation of, with Special Reference to the Utilization of Off-Peak Power—Wm. G. Allan.239
Hydrogen Ion Measurements, A Plea for Rational Interpretation of—William C. Moore 137
Hydrogen Overvoltage and Current Density in the Electrodeposition of Zinc—U. C. Tainton.....389
Hydrogen, The Production of, by the Use of Silicon and Sodium Hydroxide—E. R. Weaver 275
Hyp-Idiomorphic and Idiomorphic Structures in Electrodeposited Metal—W. E. Hughes 317
Idiomorphic and Hyp-Idiomorphic Structures in Electrodeposited Metal—W. E. Hughes 317

PAGE

Intermittent and Alternating Operation. Electric Furnace Iron and Steel—W. E. Cahill 99
Ion Measurements, Hydrogen, A Plea for Rational Interpretation of—William C. Moore 137
Iron and Steel, Electric Furnace. Intermittent and Alternating Operations—W. E. Cahill 99
Iron, Cast, as Produced in the Electric Furnace and Some of its Problems—George K. Elliott 21
Iron, Cast, The Melting of, in the Booth Rotating Electric Furnace—H. M. Williams and T. B. Terry..... 87
Iron Foundry, The Electric Furnace in the—Lyman C. Judson and Harry P. Martin 127
Iron Ore, A Comparison Between Shaft and Open Top Furnaces in the Manufacture of Pig Iron Electrically from—R. C. Gosrow..109
Iron, Synthetic and Electric Pig, Sanely Considered—Robert Turnbull. 59
Iron, Synthetic Cast, A Study of Carburization in the Manufacture of—Clyde E. Williams and C. E. Sims..... 63
Iron, Synthetic Cast—Jas. L. Cawthon, Jr..... 45
Jones, W. B.—Experiments with Alternating Current in Direct Current Electrolysis 151
Judson, Lyman C., and Harry P. Martin—The Electric Furnace in the Iron Foundry 127
Kern, Edward F., and M. Y. Chang—Conductivity of Copper Refining Electrolytes 181
Kern, Edward F.—*Discussion*.....198 *et seq.*
Lind, S. C.—*Discussion*.....301 *et seq.*
Lyon, D. A.—*Discussion*.....121 *et seq.*
MacRae, Duncan—*Discussion*.....315 *et seq.*
MacRae, Duncan—The Measurement of Pressures in Vacuum Type Electric Lamps 311
Madsen, C. P.—*Discussion*.....149, 361
Martin, Harry P., and Lyman C. Judson—The Electric Furnace in the Iron Foundry 127
McKay, Robert J.—Corrosion by Electrolyte Concentration Cells.....201
McKay, Robert J.—*Discussion*.....213 *et seq.*
Measurement of Pressures in Vacuum Type Electric Lamps, The—Duncan MacRae 311
Melting of Cast Iron in the Booth Rotating Electric Furnace, The—H. M. Williams and T. B. Terry..... 87
Members and Guests Registered at the Forty-first General Meeting... 13
Moldenke, Richard—*Discussion*.....34 *et seq.*, 39, 85, 97
Moore, W. C.—*Discussion*.....148, 211
Moore, William C.—A Plea for Rational Interpretation of Hydrogen Ion Measurements 137

PAGE

New Method of Determining the Radium Content of Carnotite Ores and Other Products of Low Activity, A—Victor F. Hess.....287
Nickel Depositing Solutions, The Acidity of—M. R. Thompson.....333
Off-Peak Power, The Electrolytic Generation of Hydrogen and Oxygen with Special Reference to the Utilization of—Wm. G. Allan.239
Open Top and Shaft Furnaces, A Comparison Between, in the Manufacture of Pig Iron Electrically from Iron Ore—R. C. Gosrow.109
Ortho-Amidophenol, Electrolytic Preparation of—O. W. Brown and J. C. Warner 225
Overvoltage, Hydrogen and Current Density in the Electrodeposition of Zinc—U. C. Tainton.....389
Oxygen and Hydrogen, The Electrolytic Generation of, with Special Reference to the Utilization of Off-Peak Power—Wm G. Allan.239
Paterson, C. C.—*Discussion*.....315 *et seq.*
Pig Iron Electrically from Iron Ore, A Comparison Between the Shaft and Open Top Furnaces in the Manufacture of—R. C. Gosrow.109
Pig Iron, Synthetic and Electric, Sanely Considered—Robert Turnbull. 59
Plea for Rational Interpretation of Hydrogen Ion Measurements, A—William C. Moore 137
Pressures in Vacuum Type Electric Lamps, The Measurement of—Duncan MacRae 311
Proceedings of the Forty-first General Meeting..... 1
Proctor, C. H.—*Discussion*.....358 *et seq,* 384, 387
Production of Hydrogen by the Use of Silicon and Sodium Hydroxide, The—E. R. Weaver 275
Radium Content of Carnotite Ores and Other Products of Low Activity, A New Method of Determining the—Victor F. Hess..287
Report of Committee on Publications..... 4
Report of Tellers of Election..... 4
Secretary's Annual Report 9
Shaft and Open Top Furnaces in the Manufacture of Pig Iron Electrically from Iron Ore, A Comparison Between—R. C. Gosrow.109
Silicon and Sodium Hydroxide, The Production of Hydrogen by the Use of—E. R. Weaver.....275
Sims, C. E., and Clyde E. Williams—A Study of Carburization in the Manufacture of Synthetic Cast Iron..... 63
Smith, Acheson—*Discussion* 125
Smith, Acheson—The Technical Man as a Citizen..... 15
Sodium Hydroxide and Silicon, The Production of Hydrogen by the Use of—E. R. Weaver.....275
Steel and Iron, Electric Furnace. Intermittent and Alternating Operations—W. E. Cahill 99
Stewart, V. T.—*Discussion* 274
Storage Batteries, A Study of Effect of Impurities on—Helen C. Gillette 217

PAGE

Stoughton, Bradley—*Discussion*.....39, 40, 82 *et seq.*, 85, 104, 136
Study of Carburization in the Manufacture of Synthetic Cast Iron, A—Clyde E. Williams and C. E. Sims..... 63
Study of Effect of Impurities on Storage Batteries, A—Helen C. Gillette 217
Study of the Throwing Power and Current Efficiency of Zinc Plating Solutions, A—W. Grenville Horsch and Tyler Fuwa.....363
Synthetic and Electric Pig Iron Sanely Considered—Robert Turnbull. 59
Synthetic Cast Iron, A Study of Carburization in the Manufacture of—Clyde E. Williams and C. E. Sims..... 63
Synthetic Cast Iron—Jas. L. Cawthon, Jr..... 45
Tainton, U. C.—Hydrogen Overvoltage and Current Density in the Electrodeposition of Zinc 389
Technical Man as a Citizen, The—Acheson Smith..... 15
Tellers of Election, Report of..... 4
Terry, T. B., and H. M. Williams—The Melting of Cast Iron in the Booth Rotating Electric Furnace..... 87
Thatcher, C. J.—*Discussion*.....212 *et seq.*, 315
Thompson, M. R.—*Discussion*.....198, 330 *et seq.*, 361 *et seq.*
Thompson, M. R.—The Acidity of Nickel Depositing Solutions.....333
Throwing Power and Current Efficiency of Zinc Plating Solutions, A Study of—W. Grenville Horsch and Tyler Fuwa.....363
Thum, Ernest—*Discussion* 106
Treasurer's Annual Report 12
Turnbull, Robert—*Discussion*.....83 *et seq.*, 86, 97, 105, 123 *et seq.*
Turnbull, Robert—Synthetic and Electric Pig Iron Sanely Considered. 59
Utilization of Off-Peak Power, The Electrolytic Generation of Hydrogen and Oxygen with Special Reference to the—Wm. G. Allan 239
Vuilleumier, E. A.—*Discussion*.....359 *et seq.*
Warner, J. C., and O. W. Brown—Electrolytic Preparation of Ortho-Amidophenol 225
Weaver, E. R.—The Production of Hydrogen by the Use of Silicon and Sodium Hydroxide 275
Williams, Clyde E., and C. E. Sims—A Study of Carburization in the Manufacture of Synthetic Cast Iron..... 63
Williams, Clyde E.—*Discussion*.....82 *et seq.*, 86
Williams, H. M., and T. B. Terry—The Melting of Cast Iron in the Booth Rotating Electric Furnace..... 87
Williams, H. M.—*Discussion*..... .....97 *et seq.*
Young, Robert J.—*Discussion*.....40 *et seq.*
Zinc, Electrodeposition of, Hydrogen Overvoltage and Current Density in the Electrodeposition of—U. C. Tainton.....389
Zinc Plating Solutions, A Study of the Throwing Power and Current Efficiency of—W. Grenville Horsch and Tyler Fuwa.....363

PERIODICAL